



Controlled/living radical polymerization in aqueous dispersed systems

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Abstract

Recent advances in the understanding and application of living/controlled radical polymerizations (L/CRP) to aqueous dispersions, including miniemulsion, emulsion, and suspension, are reviewed. The advantages of aqueous dispersions for commercializing L/CRP systems provide a powerful incentive for adapting L/CRP to dispersed systems, but there have been significant challenges posed by the inherent nature of operating in a heterogeneous environment and in confined reaction volumes. Stable-free radical polymerization (SFRP), atom transfer radical polymerization (ATRP), and reversible-addition-fragmentation-transfer (RAFT) polymerization in heterogeneous systems have all been the subject of active investigation. Developments in the chemistry of each type of L/CRP have facilitated their successful adaptation to aqueous dispersed systems. Newer types of L/CRP, including cobalt-mediated polymerization and reverse iodine transfer polymerization (RITP), have been rapidly adapted to enable their use in water-borne systems. The progress of each type of L/CRP in aqueous dispersions is discussed, along with outstanding challenges, issues, and future opportunities.

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1. Introduction

1.1. Scope of the review

The discovery of “living” or “controlled” radical polymerizations (henceforth referred to as “L/CRP”) has spurred extensive research efforts during the past decade. The ability to achieve a high degree of control over polymer microstructure under relatively mild

conditions signifies a marked increase in the ease with which structures such as di- and triblock polymers, star polymers, and comb-like graft polymers can be prepared. Prior to the advent of L/CRP, anionic polymerizations (requiring very low temperatures ($\sim -80^\circ\text{C}$), rigorous purification of reagents and careful exclusion of moisture and oxygen) were the most common route to these materials. As basic understanding of the three major types of L/CRP

(stable-free radical polymerization (SFRP), atom transfer radical polymerization (ATRP), reversible-addition-fragmentation-transfer (RAFT)) developed, so did interest in adapting these systems to aqueous dispersed environments, such as emulsion and miniemulsion polymerization. The incentives to progress to aqueous dispersions are important; many polymers made by a free radical process are polymerized in emulsion-based systems, primarily for economic reasons. Aqueous dispersions are the best alternative for large-scale production, providing excellent heat transfer, ease of mixing, process flexibility such as semi-batch addition of reagents during polymerization, and ease of handling/transporting the final latex. Widespread commercialization of L/CRP will likely require the use of aqueous dispersions.

Adapting L/CRP to emulsion-based systems has not been a simple matter however. There are a host of added complications that arise in transferring L/CRP to a dispersed environment, including issues involving partitioning of the mediating species into the aqueous phase, exit of radicals from particles, interactions of the mediating species with other components in the formulation, and poor colloidal stability. The first attempts to conduct L/CRP in aqueous dispersions logically used emulsion polymerization. However these attempts generally failed, leading to the use of miniemulsions, which have proven to be quite robust for all forms of L/CRP [1,2]. In recent years, there have been several exciting and innovative developments in L/CRP aqueous dispersions. Understanding of the interaction of the L/CRP chemistry within a colloiddally dispersed environment has progressed to the stage where processes are approaching (or have reached) commercial viability.

This review will discuss and critique progress since the earlier reviews of Qiu et al. [2] and Cunningham [1]. The review contains concise introductions to L/CRP chemistry and emulsion/miniemulsion polymerization, however it is assumed the reader is familiar with the fundamentals of L/CRP and aqueous dispersed polymerizations. Detailed descriptions of L/CRP chemistry in bulk and solution (for RAFT, ATRP, and SFRP) have been published elsewhere [3–8]. Recent reviews on L/CRP in aqueous dispersed systems are also available [9–11].

1.2. Aqueous dispersed phase polymerizations

1.2.1. Emulsion polymerization

Emulsion polymerization begins with an oil-in-water dispersion of monomer droplets in an aqueous

surfactant solution and yields a dispersion of polymer particles with mean diameters ~ 50 – 500 nm. It is widely used industrially to manufacture coatings, paints, adhesives, and resins. Monomers used in emulsion polymerization are usually sparingly soluble in water (e.g. styrene, acrylates, methacrylates). Suitable surfactants may be ionic or non-ionic, and are typically used above their critical micelle concentration (CMC). Anionic surfactants such as sodium dodecyl sulfate (SDS) or sodium dodecyl benzene sulfonate (SDBS) are most commonly used in research studies while industrial formulations commonly employ mixed surfactant systems (anionic and non-ionic) to improve colloidal stability. Initiators are usually water-soluble. Upon heating, the initiator decomposes to give aqueous radicals that propagate with monomer dissolved in the aqueous phase. After adding a few monomer units, the aqueous oligoradicals become sufficiently hydrophobic to enter micelles, thereby initiating polymerization in the micelles/particles. Particle nucleation continues until all micelles have either been nucleated or consumed to stabilize growing particles. Particles can continue to be nucleated by homogeneous nucleation as long as monomer droplets exist in the system. Particles grow by absorbing monomer from the droplets, which function as reservoirs until they are depleted, after which the remaining monomer in the particles is polymerized. Small radicals (e.g. arising from chain transfer) can exit the particles, thereby lowering the average number of radicals per particle and therefore the reaction rate. Probability of exit of a small radical depends on its water solubility and how it partitions between the particles and aqueous phase.

1.2.2. Miniemulsion polymerization

The miniemulsion process possesses some of the same features as emulsion polymerization, but the particle nucleation mechanism is quite different. Miniemulsion polymerization employs as a costabilizer a highly water-insoluble hydrophobe (e.g. hexadecane) and the initial reaction mixture is subjected to very high shear to create a dispersion of monomer droplets ~ 50 – 500 nm in diameter. The hydrophobe stabilizes monomer droplets against diffusional degradation (Ostwald ripening). Ideally, these monomer droplets all become polymer particles and no further nucleation occurs, although in practice this ideal is often not achieved and homogeneous nucleation can occur during polymerization. Surfactant concentration is usually

maintained below the surfactant CMC to avoid micellar nucleation. When the miniemulsion is heated and the water-soluble initiator thermally decomposes, the monomer droplets are nucleated by entering aqueous oligoradicals. Miniemulsion polymerization has some distinct advantages over emulsion polymerization, as it is suitable for making particles containing additives (e.g. pigments and other solids) or for copolymerizing highly water-insoluble monomers that are difficult to polymerize in emulsion because of their limited transport rate through the aqueous phase. A disadvantage of miniemulsions is the possible need to remove low molecular weight hydrophobe from the final product, but it has been shown that polymers can also perform satisfactorily as costabilizers [12]. For the interested reader, more detailed descriptions of (mini)emulsion polymerization are available [13].

2. Stable-free radical polymerization (SFRP)

2.1. Overview

SFRP employs a stable nitroxide (e.g. TEMPO; 2,2,6,6-tetramethyl-1-piperidinyloxy) to reversibly terminate macroradicals, thereby yielding a dormant chain (Scheme 1). The equilibrium is shifted strongly toward the dormant species so that the propagating radical concentration is lower than in conventional radical polymerization. Under typical reaction conditions, a dormant chain may be activated every $\sim 10^2$ – 10^3 s on average, and adds ~ 1 – 5 monomer units prior to deactivation. The deactivation step is fast, with deactivation of a propagating radical occurring $\sim 10^{-4}$ – 10^{-3} s after it is activated. Irreversible termination, which leads to dead chains and broadening of the molecular weight distribution, cannot be eliminated but under

appropriately chosen conditions its rate can be minimized. Termination also results in accumulation of nitroxide, which shifts the equilibrium toward the dormant state, thereby lowering the radical concentration and the polymerization rate. Conditions are selected so that all chains are initiated within minutes of the start of reaction, using either bicomponent systems (free radical initiator and nitroxide) or alkoxyamines. Bicomponent systems avoid unimer synthesis, but better control of the number of polymer chains is achieved with alkoxyamines. The equilibrium between active and dormant chains is sensitive to temperature, and elevated temperatures are necessary to achieve reasonable reaction rates. The general rate expression for SFRP is

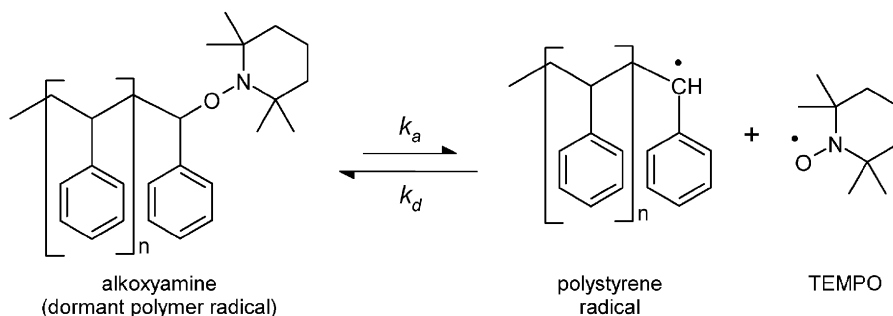
$$R_p = -d[M]/dt = k_p[M][R\cdot] \\ = k_p K_{\text{SFRP}}[M][P_n - N]/[\text{Nitroxide}], \quad (1)$$

where $R_p = -d[M]/dt$ is the rate of polymerization, $[M]_0$ the initial monomer concentration, $[M]$ the monomer concentration at any given time, k_p the propagation rate parameter, K_{SFRP} the equilibrium constant for SFRP, $[P_n - N]$ the concentration of nitroxide-terminated dormant chains, and $[\text{Nitroxide}]$ the nitroxide concentration at any given time.

Rate is inversely proportional to the nitroxide concentration, and therefore termination reactions resulting in nitroxide accumulation will suppress the polymerization rate. Degree of polymerization (DP) is given by:

$$\text{DP} = \frac{[M]_0 - [M]}{[\text{Initial chains}] + [\text{thermally generated chains}]} \quad (2)$$

If the ratio of thermally generated chains to initial chains becomes appreciable, deviation from a linear conversion versus M_n (number average molecular



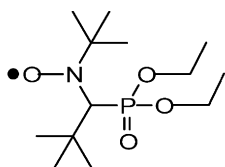
Scheme 1. Reversible deactivation of polymeric radical by TEMPO in SFRP.

weight) plot will be observed. There is no simple, reliable equation for calculating polydispersity ($PDI = M_w/M_n$; M_w is weight average molecular weight) in SFRP.

While several different nitroxides have been investigated for bulk/solution SFRP, research into heterogeneous systems has focused primarily on two nitroxides; TEMPO and *N-tert-butyl-N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (Scheme 2), better known by its trade name of “SG1” (trade name of the Arkema Group). These two nitroxides exhibit quite different behavior, both in bulk/solution and in aqueous dispersions. TEMPO is used at higher temperatures than SG1 (~ 120 – 135 °C for TEMPO, versus ~ 90 – 120 °C for SG1) because its activation rate at a given temperature is much lower than that of SG1. Thermal polymerization is therefore more of a concern for TEMPO-mediated polymerizations. There are also differences in partitioning behavior between aqueous and organic phases, sensitivity to the pH of the aqueous phase (SG1 performs better with a basic aqueous phase while TEMPO is more robust with respect to pH), rate of alkoxyamine disproportionation, and the stability of the nitroxide at reaction conditions. While TEMPO is generally a more stable radical than SG1, the limited instability of SG1 is actually beneficial as it mitigates its accumulation during polymerization, thereby facilitating the polymerization of acrylates. In view of these differences, recent progress in heterogeneous SFRP will be categorized according to nitroxide type.

2.2. TEMPO-mediated SFRP in miniemulsion

The past 5 years have seen significant advances in TEMPO-mediated miniemulsions, in both experimental capability and theoretical understanding. Previous work had demonstrated the ability to achieve only moderate conversions (~ 60 – 80%) in several hours, and many fundamental questions relating to the kinetics and heterogeneous nature of the system were not well understood [1,2,11].

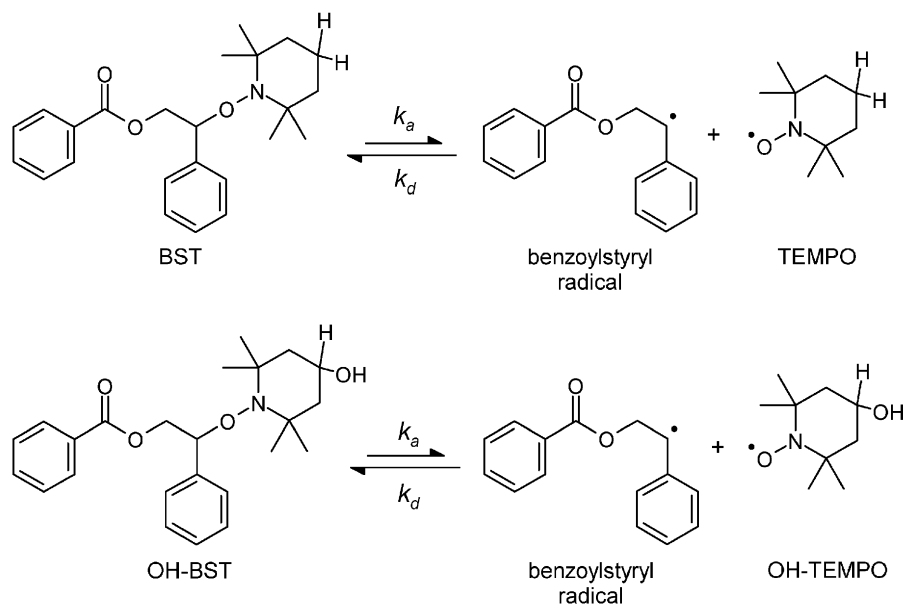


Scheme 2. Structure of *N-tert-butyl-N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1).

2.2.1. Modeling TEMPO-mediated SFRP miniemulsion polymerization

Ma et al. published a series of papers on the mathematical modeling of TEMPO-mediated styrene miniemulsion polymerization [14–17]. Experimental data was used to refine and validate the models. They separately considered alkoxyamine- [14] or persulfate-initiated [15] polymerizations in a comprehensive model, accounting for nitroxide and oligomer partitioning between phases, aqueous phase reactions, phase transfer events including entry/exit of oligoradicals and TEMPO-terminated radicals, disproportionation, and thermal polymerization. Molecular weight distributions of both living and dead chains, polymerization rate, and the fraction of living and dead polymer chains were calculated throughout the polymerization. The influence of nitroxide partitioning on the polymerization kinetics was examined by modeling systems initiated by the alkoxyamines BST and OH-BST (Scheme 3).

A mathematical model was also developed to predict the interfacial mass transfer of nitroxides in a non-reacting SFRP system [17]. Simulations were used to examine how the time required for TEMPO to achieve phase equilibrium was influenced by TEMPO diffusivity in the aqueous and organic phases, and by average droplet diameter. The analysis was extended to include the more water-soluble TEMPO derivatives 4-amino-TEMPO and 4-hydroxy-TEMPO. Predicted equilibration times were compared with the characteristic time required for the nitroxide to deactivate polymer radicals to ascertain whether the nitroxide will achieve phase equilibrium during polymerization. Under typical polymerization conditions, the characteristic radical deactivation times within particles were calculated to be more than ten times greater than equilibration times ($< \sim 10^{-4}$ s). Phase equilibrium should be established before much of the nitroxide can deactivate polymer radicals in either the aqueous or organic phases, and thus TEMPO is expected to be at phase equilibrium at all times during polymerization. Varying the nitroxide partition coefficient was predicted to change the equilibrium concentrations of nitroxide but not the time required to reach phase equilibrium. In simulations conducted for a range of average droplet diameters (100–300 nm), it was predicted that phase equilibrium would be achieved in $< 3 \times 10^{-5}$ s. However at larger droplet diameters corresponding to suspension and emulsion polymerizations, the predicted



Scheme 3. Structures of the alkoxyamines BST and OH-BST.

equilibration times are significantly greater, giving rise to the possibility of diffusion-controlled reactions.

2.2.1.1. Nitroxide partitioning effects. Monomer conversions are nearly independent of the water-solubility of the alkoxyamine (BST versus OH-BST) and its initial concentration despite the widely differing partition coefficients for TEMPO and 4-hydroxy-TEMPO [14]. The rationale for this somewhat surprising finding was elucidated using the mathematical model. 4-hydroxy-TEMPO partitions into the aqueous phase more favorably than TEMPO, which should at first appearance result in lower values of [4-hydroxy-TEMPO] in the particle phase and faster polymerization rates compared to TEMPO-mediated systems. However, the predicted organic phase concentrations of active polymer radicals were found to be nearly equal regardless of whether BST or OH-BST was used to initiate polymerization, which is consistent with the experimental data. The explanation is that thermal initiation dominates the phase partitioning behavior such that the nitroxide concentration in the particle phase exhibits little sensitivity towards the partition coefficient. Consequently, the polymerization rate is not significantly influenced by the different partitioning coefficient of the nitroxides. In the absence of thermal initiation, the model predicted both rate and radical concentration in the particle phase to be

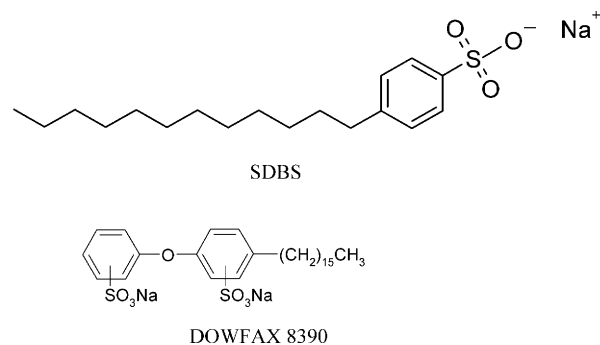
quite sensitive to the value of the partition coefficient, with the rate predicted to be significantly faster in the OH-BST-initiated systems. This prediction is consistent with the findings of Tortosa et al. [18] who reported that in the nitroxide-mediated block copolymerization of styrene and butyl acrylate in miniemulsion at 135 °C, the rate of butyl acrylate (which does not undergo thermal polymerization) polymerization was found to be significantly faster in systems employing 4-hydroxy-TEMPO compared to systems employing TEMPO. Zetterlund and Okubo [19] corroborated these findings and provided a more detailed discussion of the nature of the observed insensitivity of rate to the partition coefficient.

Alkoxyamine disproportionation was found to be responsible for terminating the majority of polymer chains in TEMPO-mediated miniemulsions. At ~60% conversion, ~70% of the dead polymer chains are formed by alkoxyamine disproportionation, while combination and disproportionation, transfer to monomer, and hydroxylamine disproportionation accounted for only 15%, 15%, and 1% of the total number of dead polymer chains, respectively.

2.2.2. Role of surfactant

A surfactant's primary role is stabilization of the polymerizing particles, and ideally it does not further affect the course of polymerization. There are limited choices for surfactant at higher

temperatures. Sulfates, which are commonly used at temperatures $<100\text{ }^{\circ}\text{C}$, undergo hydrolysis at higher temperatures and are generally not suitable. Sulfonates have excellent hydrolytic stability and have been proven to function effectively at elevated temperatures ($100\text{--}140\text{ }^{\circ}\text{C}$). The two most commonly used in SFRP miniemulsions are sodium dodecyl benzene sulfonate (SDBS) and DOWFAX 8390 (Dow Chemical Inc.) (Scheme 4). Neither surfactant is “pure”. SDBS is available only in a technical grade (usually $\sim 80\%$) while DOWFAX 8390 is a mixture of mono- and di-hexadecyl disulfonated diphenyloxide sodium salts. Lin et al. [20,21] examined the effect of [SDBS] and [DOWFAX 8390] on TEMPO-mediated styrene miniemulsions, and found that rates were influenced, often significantly, by [SDBS] while [DOWFAX 8390] had minimal effect on the rate. Increasing [SDBS] resulted in increased rates of polymerization, although PDI and the polymer chain livingness were not negatively impacted. The observed increase in rate is ultimately attributable to reduced [TEMPO], although the exact nature of that reduction remains uncertain. Possible explanations include direct consumption of TEMPO by reaction with SDBS or the generation of additional radicals in the presence of SDBS. However, purification of the SDBS did not alter its behavior in the polymerization. There was a small increase in the number of chains as [SDBS] was increased, which is consistent with generation of additional radicals. Subsequent work published by Osti et al. [22] demonstrated that SDBS was able to generate radicals in the presence of reducing agents (ascorbic acid), giving more credence to the possibility that radical generation is the most likely explanation for the increase in rates during TEMPO-mediated miniemulsion polymerizations.



Scheme 4. Structures of the surfactants SDBS and DOWFAX 8390.

Pan et al. [23] examined the effects of [DOWFAX 8390] on TEMPO-mediated styrene miniemulsions. Using a polystyrene macroinitiator with hexadecane as costabilizer, they produced particles varying in diameter from ~ 50 to ~ 160 nm by varying [DOWFAX 8390] from 15 to 1.25 mM. $\log N_p$ (L^{-1} of aqueous phase) varied with \log [DOWFAX 8390]^{1,43}. There was evidence of homogeneous nucleation. Despite the significant effect of [DOWFAX 8390] on particle number and diameter, minimal effects were observed on the rate of polymerization, M_n and PDI.

2.2.3. Achieving high conversions in TEMPO-mediated SFRP miniemulsions

Nitroxide-scavenging additives can be used to increase polymerization rate, although the role of various additives may be more complex than just simple reaction with nitroxide. Cunningham et al. [24] used camphorsulfonic acid (CSA) with moderate success in TEMPO-mediated styrene miniemulsions. CSA addition was not as effective however in miniemulsion as it was in bulk. CSA, because it is solid, must be added all at the beginning of the polymerization (dissolved in styrene) although ideally, a nitroxide scavenger would be added gradually during polymerization to offset the accumulation of nitroxide and consequent rate depression that occurs due to the persistent radical effect [25]. Lin et al. [26,27] pursued this approach using semi-batch addition of ascorbic acid as the nitroxide scavenger in TEMPO-mediated styrene miniemulsions. Through appropriate choice of ascorbic acid addition rate, the polymerization rate was significantly enhanced. High conversions ($>98\%$) were obtained in 2–3 h (faster than industrial styrene polymerizations) while PDI remained <1.3 (Fig. 1). Fluorescence analysis of the chain ends revealed that livingness was actually enhanced when the rate was increased, as the reduction in reaction time led to less dead chain formation through disproportionation.

2.2.4. Low-temperature TEMPO-mediated SFRP

Although TEMPO is typically used in the range of $\sim 120\text{--}135\text{ }^{\circ}\text{C}$, Ng et al. [28] demonstrated it was feasible to use temperatures $\sim 100\text{ }^{\circ}\text{C}$ through judicious use of a nitroxide scavenger. In their experiments, ascorbic acid was added in semi-batch mode to a styrene miniemulsion polymerization. Although the polydispersities were broader than values achieved at higher temperatures, the polymer

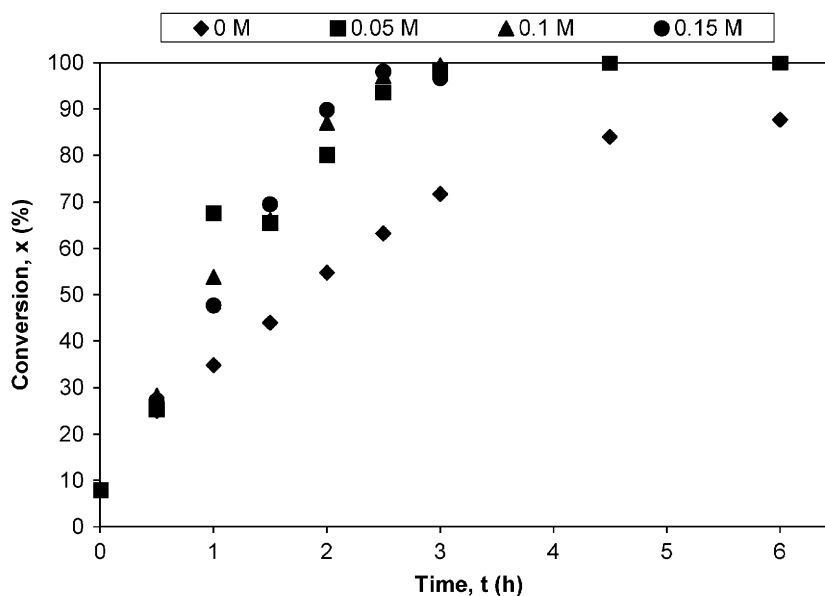


Fig. 1. Conversion-time profiles for semi-batch addition of ascorbic (at various concentrations) to TEMPO-mediated styrene polymerizations ($T = 135^\circ\text{C}$) [26,27].

livingness was excellent, as witnessed by evolution of the molecular weight distributions and the use of fluorescence measurements [29]. TEMPO cannot usually be used at lower temperatures because: (1) its activation rate is fairly slow below $\sim 115^\circ\text{C}$ and (2) thermal initiation is very slow at these temperatures, which leads to TEMPO accumulation and subsequent depression of the polymerization rate. By carefully adding in ascorbic acid, the excess TEMPO is consumed and the TEMPO concentration can be maintained at a level that affords reasonable rates while maintaining a living system. An advantage of working at lower temperatures with TEMPO is that the disproportionation rate is much less at lower temperatures, as revealed by the modeling work of Ma et al. [14].

2.2.5. Crosslinking in TEMPO-mediated miniemulsions

With the emphasis in preparing narrow MWD polymers for use primarily in di- and triblock polymers, comparatively little attention has been given to understanding how L/CRP systems behave when crosslinked, and whether there may be advantageous properties in living networks. In a series of papers, Okubo and Zetterlund explored the styrene/divinylbenzene (ST/DVB) system [30–32]. While it has been observed that bulk kinetics for L/CRP systems are often similar to miniemulsion

kinetics (see the section on “Compartmentalization” later in this section for more discussion on this topic), pronounced differences were observed in the kinetics and crosslinking behavior of the TEMPO-mediated styrene/divinylbenzene system [30,32]. Using a TEMPO-terminated polystyrene macroinitiator, Zetterlund and Okubo conducted bulk and miniemulsion polymerizations at 125°C , using 1% DVB with respect to styrene. No hydrophobe was added. Particle diameters of ~ 50 and ~ 500 nm were made in miniemulsion. The miniemulsions displayed faster polymerizations than the bulk; furthermore the miniemulsion with smaller particles was faster than when large particles were made. Conversion of the pendant vinyl groups and crosslink densities also differed between the bulk and miniemulsion systems. Miniemulsion polymerizations showed slower conversion of the pendant vinyls and considerably lower crosslink densities, signifying lower incorporation of DVB. A suggested explanation is DVB partitioning into the aqueous phase; although DVB has lower water solubility than styrene, the fraction of DVB present in the aqueous phase would be large compared to the fraction of styrene in the aqueous phase [32]. However, further experiments in which hydrophobe (tetradecane) and/or solvent (toluene) were added to the miniemulsions and higher DVB concentrations were used (8.2% with respect to styrene) did not

show differing consumption rates of DVB and styrene [31].

2.2.6. TEMPO-mediated acrylate polymerization

There have been limited successes of acrylate polymerizations mediated by TEMPO. Block copolymers (styrene-*b*-butyl acrylate) made in TEMPO-mediated miniemulsions were reported by Tortosa et al. [18] and Keoshkerian et al. [33]. Chain extension of the initial polystyrene block proceeded well, with high re-initiation efficiency of the first block and final polydispersities ~ 1.3 . Keoshkerian et al. [33] were able to obtain high conversion ($>99\%$) in both blocks by using ascorbic acid addition. More recently, Georges et al. [34,35] studied the TEMPO-mediated homopolymerization of *n*-butyl acrylate in bulk [34] and miniemulsion [34,35]. Nitroxide-mediated acrylate polymerizations tend to be limited to low conversions ($<10\%$) as nitroxide accumulates due to the persistent radical effect. This is not as serious a problem for nitroxides like SG1 that have some inherent instability that acts to mitigate this effect. TEMPO however is quite stable and therefore has proven to be a major challenge for acrylates. Georges et al. [34] used semi-batch ascorbic acid addition (or its oil-soluble derivative, ascorbic acid 6-palmitate) to control the excess TEMPO concentration in demonstrating that reasonable conversions could be achieved in either bulk or miniemulsion. In miniemulsion, 53% conversion was obtained in 6 h, yielding $M_n = 18.5$ kg/mol with PDI = 1.35.

2.3. TEMPO-mediated SFRP in emulsion

True TEMPO-mediated emulsion polymerization has proven to be an elusive challenge. Early attempts at conducting TEMPO-mediated emulsion polymerization were unsuccessful, yielding living polymer but also severe coagulum [1,2,11]. The reason(s) for the colloidal stability problems are not fully understood. It was previously thought that a combination of factors likely contributed to the coagulum, including the particle nucleation step and polymerization in the droplets. (Droplet polymerization is an undesired consequence of conducting the reaction at higher temperatures where thermal polymerization occurs.) Szkurhan and Georges [36] concluded that while thermal polymerization in the droplets was a contributor to colloidal instability, avoiding it (for example by using *n*-butyl acrylate as

monomer) does not necessarily provide stable latexes.

Techniques have been created to develop modified SFRP emulsion polymerization processes. Szkurhan and Georges [36] reported a nanoprecipitation technique in which seed particles are created in situ by dispersing an acetone-containing solution of TEMPO-terminated polystyrene macroinitiator into an aqueous phase containing the non-ionic surfactant PVA (polyvinylalcohol). The acetone was allowed to evaporate, giving a stable dispersion of seed particles. The seed latex was then swollen with monomer and polymerized to yield a stable latex with mean particle diameters ~ 400 – 500 nm. The authors state that the extent of seed particle swelling with monomer was chosen to prevent the formation of droplets. Typically 10 mL of styrene was added to 1 g of polystyrene macroinitiator. While this much monomer exceeds the swelling capacity of high molecular weight seeds, the low molecular weight oligomer used for their seed particles ($M_n \sim 3300$ g/mol) is expected to have increased swelling capability, possibly enough to absorb all of the added monomer, although it is possible some droplets were present in the early stages of polymerization. Curiously this approach was not amenable to semi-batch addition of the monomer; a bimodal particle size distribution (mean diameters ~ 400 and ~ 900 nm) was observed as was as a bimodal molecular weight distribution when the monomer was fed in under starved conditions. Surfactant choice was critical to the formation of a stable seed, with only PVA giving stable emulsions. Szkurhan and Georges also detailed several unsuccessful approaches at SFRP emulsion polymerization using a variety of different procedures. Analogous techniques were also reported for RAFT [37] and ATRP [38].

2.4. SG1-mediated polymerization in miniemulsion

2.4.1. Polymerization using a monomer-soluble SG1-based alkoxyamine

While studies on TEMPO-mediated polymerizations have been mostly limited to styrenic monomers, the versatility of SG1 has more readily allowed polymerization of styrene and acrylates in miniemulsion [39,40]. SG1 (Scheme 2) is structurally different than TEMPO, being an acyclic β -phosphonylated nitroxide that yields faster kinetics than TEMPO. *n*-Butyl acrylate is a “fast” monomer with a high propagation rate constant that makes controlling its polymerization difficult, and

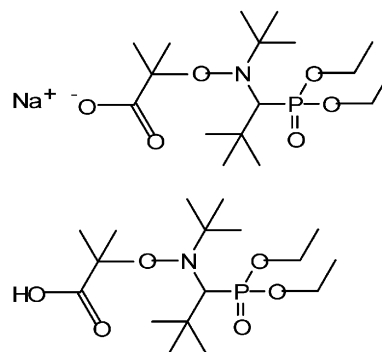
consequently additional SG1 is required to maintain a controlled polymerization. Farcet et al. [39] found the initial ratio of [SG1]: [MONAMS] (the SG1-based alkoxyamine) was critical in determining the polymerization rate. A ratio of [SG1]: [MONAMS] ~ 0.035 –5 was sufficient to provide good control, although the optimal ratio is temperature dependent. Lower ratios result in higher rates but broad molecular weight distributions, while higher ratios suppress the rate. Conversions $> 70\%$ were obtained with $M_n \sim 25$ –30 kg/mol and PDI ~ 1.4 –1.6. Particle sizes tended to be somewhat large (~ 400 –650 nm) with a broad size distribution but colloidal stability was reported to be good.

2.4.2. Polymerization using a water-soluble SG1-based alkoxyamine

Earlier work from the Charleux laboratory had used monomer-soluble SG1-based alkoxyamines in conducting miniemulsions but more recent work has centered on the use of a water-soluble SG1-based alkoxyamine, known as MAMA or by its current trade name “BlocBuilder” (Arkema Group) [40] (Scheme 5). BlocBuilder contains a carboxylic acid moiety that imparts water solubility. At $\text{pH} > \sim 5.5$, it exists in the ionized (sodium salt) form while at lower pH it remains in acid form. This study, although conducted in miniemulsion, provided the initial knowledge for subsequent development of an emulsion polymerization process (described in the following section). BlocBuilder has an unusually high dissociation rate constant and does not require additional SG1 to give a controlled polymerization, even for *n*-butyl acrylate. Although the alkoxyamine is soluble in the aqueous phase, upon adding a few monomer units it becomes sufficiently hydrophobic to enter droplets or particles (similar to water-soluble initiators in conventional (mini)emulsion polymerization) where it mediates the polymerization. High initiation efficiencies were observed for *n*-butyl acrylate but not for styrene. This was attributed to low oligoradical entry rates from the aqueous phase due to slow aqueous phase styrene polymerization. However, addition of small amounts of methyl acrylate significantly improved the efficiency by increasing the propagation rate of oligomeric radicals in the aqueous phase.

2.5. SG1-mediated polymerization in emulsion

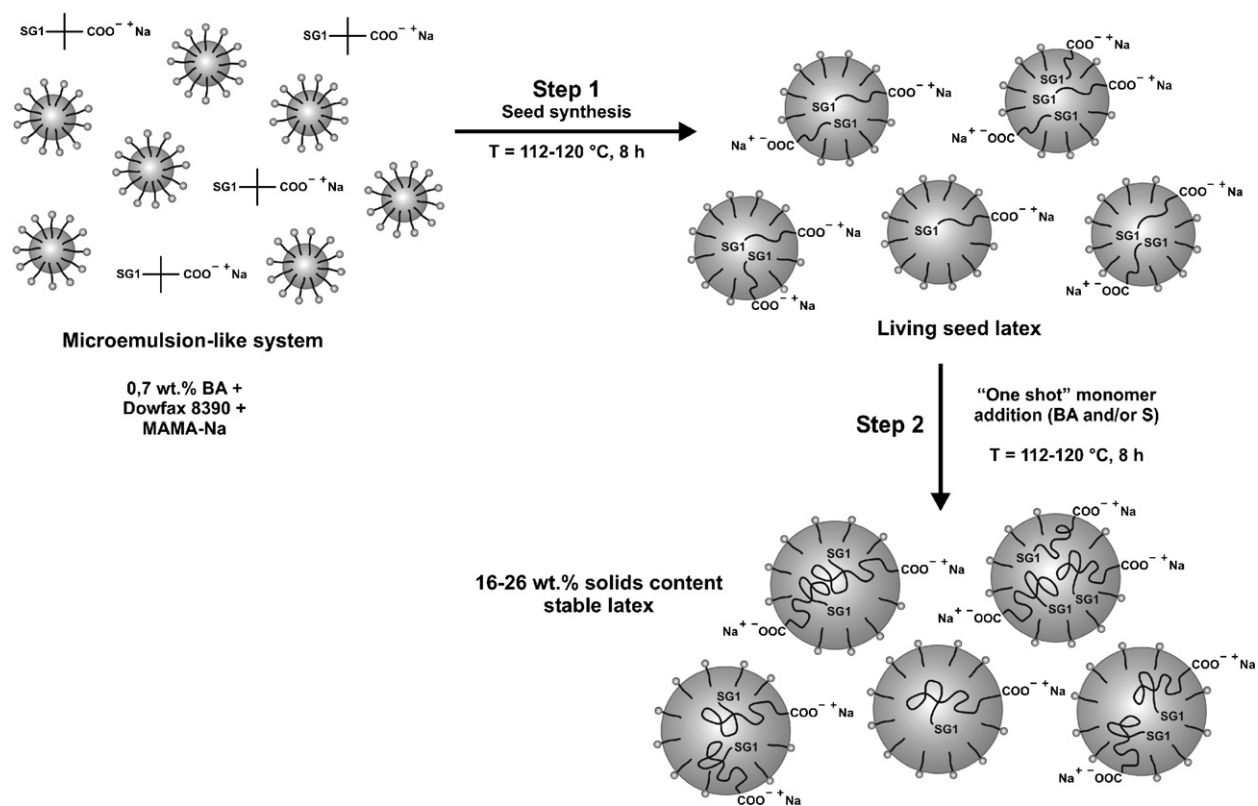
Considerable progress has been made in developing an emulsion polymerization process using the



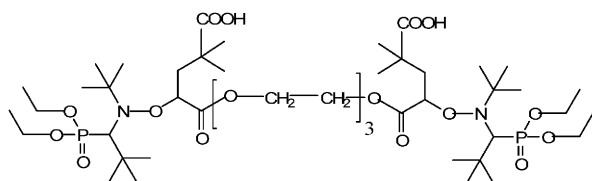
Scheme 5. The SG1-based alkoxyamine MAMA (BlocBuilder) in ionized and non-ionized forms.

water-soluble SG1-based alkoxyamine “BlocBuilder”, using styrene and/or *n*-butyl acrylate [41–44]. BlocBuilder allows effective aqueous phase initiation, an important prerequisite for an emulsion polymerization process. The approach taken has been to first prepare a low molecular weight seed latex (typically ~ 150 –250 nm in diameter) with low solids content ($< 1\%$). The seeds are then swollen with monomer and polymerized to yield particles in the 300–600 nm range, depending on the conditions used, with solids contents ~ 15 –25% (Scheme 6). Good control over the molecular weight is achieved, with the observed behavior similar to that of previous SG1-mediated polymerizations in miniemulsion. The use of a seed preparation step is crucial in that it eliminates monomer droplet formation early in the polymerization.

In addition to use of the monofunctional BlocBuilder, its difunctional derivative DIAMA was prepared and also studied for emulsion polymerization (Scheme 7) [43,44]. Although the anionic surfactant DOWFAX 8390 was used, the additional contribution of the carboxylates from the difunctional derivative proved important to maintaining colloidal stability, enabling a significant reduction in particle size (and narrower distribution) compared to latexes prepared using the monofunctional BlocBuilder. In addition to the respective homopolymers, a triblock (styrene–butyl acrylate–styrene) was also made using the difunctional alkoxyamine. This process was further refined using a semi-batch monomer addition mode after preparation of the seed latex [44]. The refined process has a considerably shortened overall process time compared to earlier efforts, approaching that of industrial processes.



Scheme 6. SFRP two-step emulsion polymerization process, initiated with MAMA. Reproduced with permission [44].



Scheme 7. The SG1-based alkoxyamine DIAMA.

2.6. Compartmentalization in TEMPO-mediated (mini)emulsions

Compartmentalization in conventional emulsion polymerization gives higher reaction rates and higher molecular weights compared to bulk/solution processes by reducing the effective termination rate, since macroradicals are physically isolated from each other in small reaction volumes. Theoretical considerations [45] and limited experimental studies in miniemulsions [23,46–49] have previously indicated that in reversible termination systems (ATRP, SFRP), compartmentalization effects do not exist, although theoretical modeling studies suggested they may exist at sufficiently small particle size [50–52]. The rationale for the observed absence of

compartmentalization effects in SFRP (and ATRP) is that the primary chain-stopping event is deactivation by nitroxide, the rate of which is not affected when the polymerization is conducted in smaller particles. In contrast, in a conventional (mini)emulsion polymerization, termination is the primary chain-stopping event, and its rate is reduced as particle size is decreased. Charleux [50] used a Smith-Ewart approach for macroradical segregation in studying the SG1-mediated polymerization of styrene. Butte et al. [51] accounted for segregation of the nitroxide (TEMPO) and propagating radicals, and then Zetterlund and Okubo [52] later extended Butte's model in examining compartmentalization in SFRP. Charleux, Butte, and Zetterlund all predicted that compartmentalization effects should be evident for SFRP, although the nature of their predictions varied due to the different approaches used.

Maehata et al. [53] recently performed TEMPO-mediated styrene miniemulsion polymerizations in which the weight average particle diameter varied from ~50 to 180 nm. Experimental data showed particle size effects did exist, influencing both the

rate of polymerization and polymer chain livingness, and to a lesser extent polymer chain concentration. Smaller particles showed lower rates of polymerization than larger particles. Additionally, the rate and livingness of bulk polymerizations were found to differ from miniemulsion polymerizations, with the bulk polymerization being faster. Higher livingness was preserved in smaller particles.

The reduced rate in smaller particles may result from a combination of factors. Geminate recombination of thermally generated radicals could lead to reduced thermal initiation rates and thus a lower overall polymerization rate [51,52]. Reduction of rate by geminate termination of thermally generated radicals was also postulated by Pan et al. [48], who provided experimental data showing reduced rates in TEMPO-mediated styrene miniemulsions compared to bulk polymerization. Zetterlund and Okubo also emphasized the role of enhanced deactivation of radicals within a small volume that would result in decreasing rates as particle size decreases. Enhanced deactivation is predicted to reduce termination rates and therefore increase livingness in smaller particles.

3. Atom transfer radical polymerization (ATRP)

3.1. Overview

ATRP, whose origins lie in atom transfer radical addition chemistry, relies on the transfer of a halide atom from a catalyst/ligand complex to a propagating macroradical (Scheme 8). Copper is the most commonly used metal for the catalyst. A transition metal complex in its lower oxidation state (e.g. CuBr/ligand) activates a halide-terminated polymer chain (or alkyl halide initiator) to yield a radical and the catalyst complex in a higher oxidation state (e.g. CuBr₂/ligand). The ligand plays a critical role in determining the reactivity of the catalyst complex towards various monomers as well as affecting its solubility in the reaction medium. Deleterious reactions of the catalyst are a potential concern, and can include hydrogen abstraction (e.g. from

monomers or solvents), reaction with monomers containing acid groups, and of particular concern in emulsion-based system, reactions with anionic surfactants. ATRP does not require high temperatures, and is much more versatile than SFRP in the range of monomers it can polymerize.

ATRP has seen dramatic advances made in recent years with regards to its suitability for, and performance in, dispersed systems. Advances in SFRP and RAFT systems have progressed primarily with respect to process advances related to better understanding of how each particular chemistry behaves in a multi-phase environment. ATRP however has undergone a series of more significant variations in its basic chemistry, particularly with regards to how the polymerization is initiated, that have facilitated its adaptation to aqueous dispersions. In particular the recent advent of activator generated by electron transfer (AGET) [54] provides a more robust system, and the use of a redox initiation system has enabled synthesis of living polymer with $M_n \sim 1$ million [55], significantly enhancing previous capabilities. The expansion of miniemulsion ATRP to include simultaneous use of different polymerization mechanisms was recently reported for tandem ring-opening metathesis polymerization (ROMP) and ATRP of MMA and norbornene [56].

In bulk and solution ATRP using alkyl halide initiators, the theoretical degree of polymerization and polydispersity are given by Braunecker and Matyjaszewski [3]:

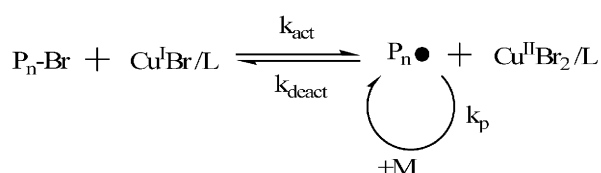
$$DP = \frac{[M]_0 - [M]}{[RX]_0}, \quad (3)$$

$$PDI = 1 + \frac{1}{DP_n} + \left(\frac{[RX]_0 k_p}{k_{\text{deact}} [Mt^{n+1}X/L]} \right) \left(\frac{2}{\text{Conv} - 1} \right). \quad (4)$$

The rate of polymerization is given by

$$R_p = -d[M]/dt = k_p [M] K_{\text{ATRP}} [RX] \times [Mt^n/L] / [Mt^{n+1}X/L], \quad (5)$$

where k_{deact} is the deactivation rate parameter, K_{ATRP} the equilibrium constant for ATRP, $[RX]$ the concentration of halide-terminated dormant chains, $[Mt^n/L]$ the concentration of activating transition metal/ligand complex, and $[Mt^{n+1}X/L]$ the concentration of deactivating transition metal/ligand complex.



Scheme 8. Simplified reaction scheme for ATRP.

Note that the rate depends on the ratio of the activator to deactivator concentrations (i.e. $[\text{Cu(I)}]:[\text{Cu(II)}]$), and not on the absolute transition metal concentration.

3.2. ATRP in miniemulsion

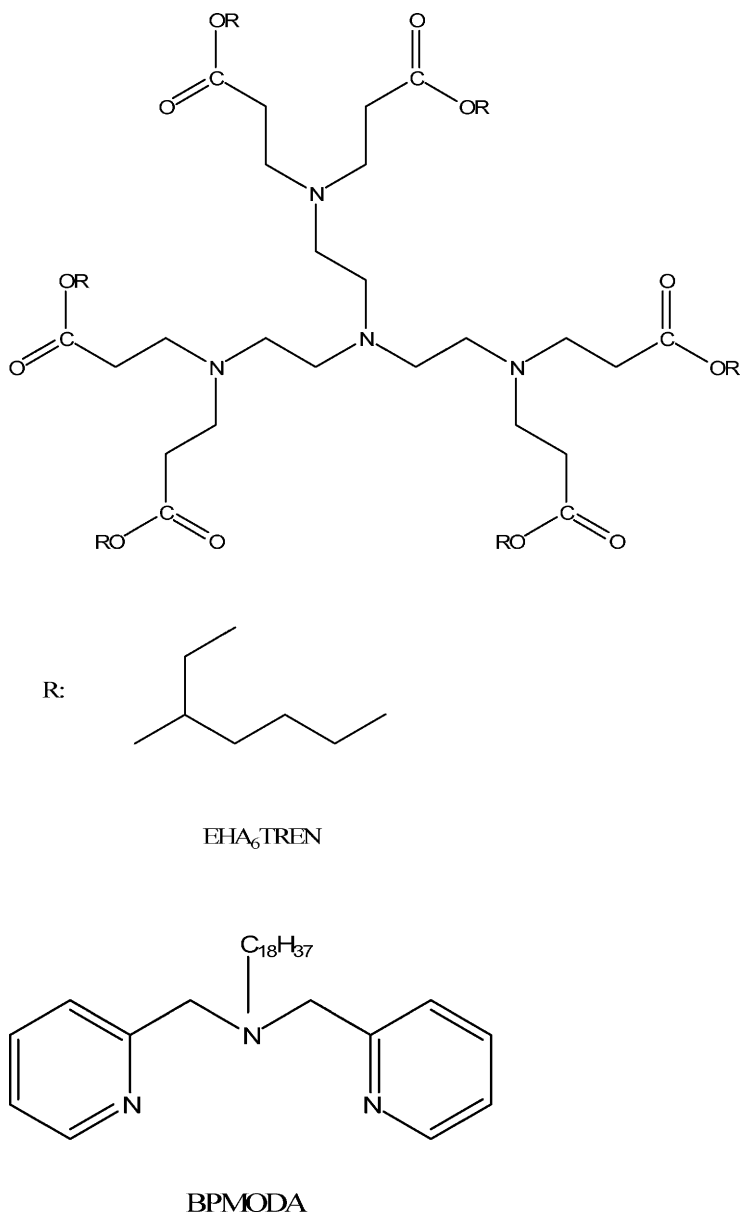
3.2.1. Reverse ATRP

Earlier aqueous-based ATRP publications attempted forward ATRP and used bipyridine ligands, a system that worked well in bulk and solution but fared poorly in aqueous systems. A series of innovations has dramatically improved the process [57]. The direct (forward) ATRP process was shown to be unsuitable for aqueous-based processes because of the sensitivity of the Cu(I) species to air. Therefore reverse ATRP was employed, as it uses Cu(II) which is far more tolerant of exposure to air when the miniemulsion is passed through a high shear mixing device such as a microfluidizer or sonication. Further innovations included the use of more hydrophobic bipyridine-based ligand 4,4'-di(5-nonyl)-2,2'-bipyridyl (dNbp) which significantly improved the retention of the catalyst in the particle phase and minimized partitioning into the aqueous phase. The development of highly active, hydrophobic ligands such as EHA₆-TREN or BPMODA (Scheme 9) offer much improved performance for reverse ATRP in miniemulsion [57]. It should be noted that a further requirement of ligands for aqueous dispersions is that they must form fully soluble catalyst complexes in the chosen monomer, unlike bulk/solution ATRP where heterogeneous catalysts are acceptable. Reverse ATRP with these improvements showed much better overall performance in the polymerization of *n*-butyl methacrylate [58]. Surfactant (Brij 98) concentrations were reduced to 0.58 wt% based on water, and solids contents raised to 20 wt%. PDIs ranged from ~1.4 to 1.6, higher than commonly achieved in bulk, but this is a common phenomenon in aqueous-based L/CRP. Choice of free radical initiator is important in that initiators with low decomposition rates will give broader molecular weight distributions and longer induction periods. Choice of the Cu(II) concentration is also critical, and often not simple to determine a priori. Because the efficiency of the free radical initiator depends on the particular reaction conditions, the amount of Cu(II) required will also vary. Excess Cu(II) prolongs the induction period, while insufficient Cu(II) concentrations

sacrifice control and livingness. Furthermore it is known that even with hydrophobic ligands, not all of the catalyst complex can be prevented from partitioning into the aqueous phase. A further complication is that the Cu(I) and Cu(II) species exhibit different partition coefficients [57]. Many of the challenges with reverse ATRP were resolved by development of the simultaneous normal and reverse initiation (SNRI) process, discussed in the following section.

3.2.2. SNRI ATRP

SNRI preserves the use of the less oxygen sensitive Cu(II) catalyst while solving the problem of somewhat unpredictable initiation efficiency that is experienced with reverse ATRP. In SNRI, the number of chains is determined primarily by the concentration of alkyl halide. A small amount of free radical initiator is also added (a ~5:1 ratio of alkyl halide to initiator is employed). The activating Cu(I) species is generated in situ by reduction of the Cu(II) to Cu(I) as the free radical initiator decomposes. In a series of papers [59–61], Matyjaszewski demonstrated the suitability of the SNRI process for polymerization of *n*-butyl methacrylate, *n*-butyl acrylate, and styrene. Three different hydrophobic, high activity ligands were assessed; a hexasubstituted TREN ligand (EHA₆-TREN), a picolylamine ligand (BPMODA), and a substituted terpyridine (tNtpy). There were differences observed in the performance of the various ligands, but through appropriate selection of monomer, ligand and Cu(II) concentration, well-controlled polymerizations were obtained, with PDIs (~1.2–1.3) lower than obtained with reverse ATRP. A typical $[\text{EBiB}]_0:[\text{Cu(II)}]_0$ ratio (EBiB; ethyl 2-bromoisobutyrate) was 1:0.2, reflecting a relatively low $[\text{Cu(II)}]$. The technique was extended to linear and star-shaped block copolymers [60], as well as gradient copolymers [61]. Evaluation of the block polymers by two-dimensional chromatography showed that while the purity was good, there was evidence of homopolymer contamination, presumed to arise from the small amount of free radical initiator. The evolution of the SNRI process represents a dramatic improvement over prior work. Reduction in the amount of copper through use of highly active ligands, use of the less air-sensitive Cu(II), better control of the molecular weight distribution, reduced induction periods, and lower surfactant concentrations make SNRI a more robust aqueous ATRP process.

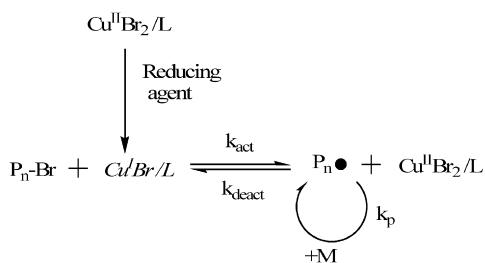


Scheme 9. ATRP ligands EHA₆-TREN and BPMODA, commonly used in miniemulsion systems.

3.2.3. AGET ATRP

As noted above, a limitation of the SNRI process is the unavoidable contamination by homopolymer of any block or star polymer structures. Because of the relatively low concentration of homopolymer arising from the radical initiator, this may be tolerable in many industrial processes. However, a solution was found that altogether eliminates use of a free radical initiator while still allowing use of the less air-sensitive Cu(II) [54,62]. AGET ATRP (Scheme 10) utilizes a reducing agent to convert

Cu(II) to Cu(I), instead of relying on radicals from initiator decomposition. The reducing agent can also scavenge oxygen, increasing the tolerance of the system to air, although the presence of oxygen will increase the amount of reducing agent required in the formulation. Ascorbic acid was used as the reducing agent in miniemulsions because of its water solubility. The concentration of ascorbic acid is critical to the outcome of the process. Best results are obtained when the ratio of ascorbic acid:Cu(II) varies from ~0.1 to 0.5:1 (ascorbic acid reduces two



Scheme 10. Proposed reaction scheme for AGET ATRP. $\text{Cu}^{\text{I}}\text{Br}/\text{L}$ is not initially present, but is generated in situ by reduction of $\text{Cu}^{\text{II}}\text{Br}_2/\text{L}$ [54,62].

equivalents of $\text{Cu}(\text{II})$, with higher ratios required if air is present. In the miniemulsion polymerization of *n*-butyl acrylate initiated by EBiB, well-controlled polymerizations were obtained with final $\text{PDI} \sim 1.2$. Linear block and three-arm star copolymers (methyl acrylate-*b*-styrene) were also prepared. The $[\text{EBiB}]:[\text{Cu}(\text{II})]$ ratios used in these studies was 1:~0.5, higher than for the SNRI experiments (1:~0.2).

3.2.4. High molecular weight polymer via reverse ATRP

Most publications dealing with ATRP, especially with aqueous systems, have yielded $M_n < \sim 80$ kg/mol, with the typical M_n values being much lower. Simms and Cunningham recently showed that ATRP is suitable for preparing much higher molecular weights in miniemulsion [55]. Using a redox initiation system (ascorbic acid/hydrogen peroxide) with a $\text{CuBr}_2/\text{EHA}_6\text{-TREN}$ catalyst, they were able to produce poly(*n*-butyl methacrylate) with $M_n \sim 10^6$ g/mol and $\text{PDI} \sim 1.25$. Conversions $> 80\%$ were achieved in ~ 8 h, with mean particle diameters ~ 100 nm. A control run using the free radical initiator VA-044 gave $M_n \sim 64$ kg/mol. The evolution of the molecular weight distributions showed excellent livingness, even at $M_n > 800,000$ g/mol (Fig. 2). Kinetic analysis showed that the apparent rate constant normalized by the number of chains increased significantly for those experiments that gave higher M_n (i.e. lower chain numbers), implying that the equilibrium constant and/or the ratio $\text{Cu}(\text{I})/\text{Cu}(\text{II})$ varied with the number of chains in the system. This seems to be contrary to our current understanding of ATRP. The paradox of being able to produce such high molecular weights and low polydispersities at reasonably high reaction rates has not yet been resolved, although it suggests that compartmentalization effects may be present.

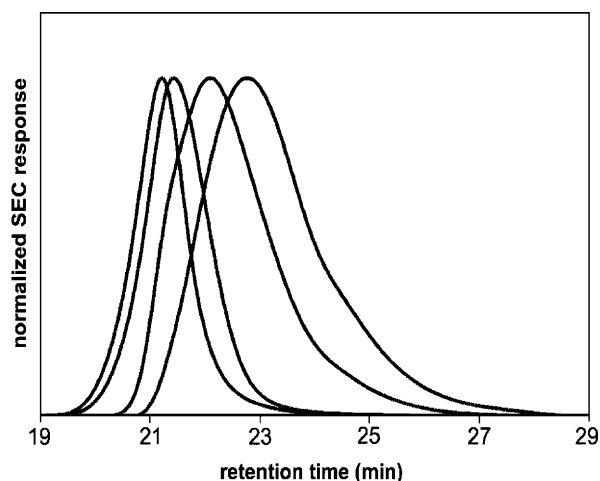


Fig. 2. Size exclusion chromatography (SEC) traces for the reverse atom transfer radical polymerization of butyl methacrylate (BMA) at 60°C in miniemulsion. $[\text{Brij } 98]:[\text{hexadecane}] = 10:3.8$ wt% based on monomer; 15% solid content; $[\text{BMA}]_0:[\text{copper}(\text{II}) \text{ bromide tris}[2\text{-di}(2\text{-ethylhexyl acrylate)aminoethyl] \text{ amine}]_0:[\text{hydrogen peroxide}]_0:[\text{ascorbic acid}] = 400:1:0.5:0.25$ (exp 8); Conversion increases from right to left; conversion = 11%, number-average molecular weight (M_n) = 222500, polydispersity index (PDI) = 1.56; conversion = 23%, $M_n = 345000$, $\text{PDI} = 1.47$; conversion = 74%, $M_n = 859000$, $\text{PDI} = 1.24$; conversion = 83%, $M_n = 989900$, $\text{PDI} = 1.24$. [55].

However the initiation itself can exhibit complex behavior, with the ascorbic acid acting not only as part of the redox initiation pair, but also as a reducing agent for the $\text{Cu}(\text{II})$ [55].

3.3. ATRP in emulsion

Eslami and Zhu [63] studied the emulsion ATRP of 2-ethylhexyl methacrylate, using EBiB as initiator and $\text{CuBr}/4,4'\text{-di}(5\text{-nonyl})\text{-2,2'}\text{-bipyridil}$ (dNbpy) as the catalyst. Five surfactants were studied, with Tween 80 and Brij 98 yielding the most promising results. They found that while the polymerizations were generally well-controlled, colloidal stability was a major issue. They found narrow operating windows and encountered severe problems with coagulum formation. Block copolymers of 2-ethylhexyl methacrylate and methyl methacrylate were also made using a bifunctional initiator [64]. In both studies, excess $\text{Cu}(\text{II})$ was required to achieve good control, but too much resulted in excessive coagulum formation. Significant difficulties were also observed using reverse ATRP [65].

Seeded ATRP emulsion polymerization was studied as a method to prepare block copolymers

[66,67]. *i*-Butyl methacrylate was the seed monomer, and styrene was added to form the second block. (Miniemulsion polymerization was used to prepare the seed latex which was subsequently swollen with a second monomer.) Utilizing the CuBr/dNbpy catalyst system with EBiB initiator, a poly(*i*-butyl methacrylate) macroinitiator was used in the miniemulsion step. The miniemulsion step proceeded reasonably well, but polymerization of the second styrene block was slow and final styrene conversion remained low (~40%), even after 96 h, although thin layer chromatography indicated the block copolymers were fairly pure. The formation of onion skin type morphologies was also seen in transmission electron micrographs, with individual layer thicknesses ~19 nm. Although the living nature of these polymerizations was generally preserved, the primary difficulties again resided with the colloidal stability aspects that balanced often high Tween 80 concentrations against acceptable particle size and PDI.

Chan-Seng and Georges [38] used a seeded nanoprecipitation technique first developed for emulsion SFRP in the ATRP of styrene. Using the hydrophobic BPMODA as ligand, 1-phenylethylbromide as initiator and PVA or Brij 98 as stabilizer, they were able to achieve reasonable results, although the process was more challenging and sensitive than with SFRP. Considerable difficulties were encountered during various experimental stages, which the authors discuss in detail. The M_n of the macroinitiator used in the seed was found to critically affect the latex stability, with $M_n < 4000$ g/mol required for stable latex formation.

Emulsion ATRP remains a difficult process that has not proven to be robust, with severe colloidal stability problems being the most critical issue. The greatest promise for an emulsion ATRP process appears to be the recently discovered *ab initio* process based on an initial microemulsion polymerization [68,69], which is discussed in the following section.

3.4. ATRP in microemulsion and development of an *ab initio* emulsion polymerization process

Microemulsions are thermodynamically stable, transparent oil–water dispersions. Microemulsion polymerizations can be used to produce particles ~20–40 nm, much smaller than usually encountered in macro- or miniemulsions [70,71]. Min and Matyjaszewski [68] extended their miniemulsion

ATRP to microemulsion. Basing their formulations on miniemulsion work, they selected Brij 98 as surfactant, BPMODA as ligand, and methyl methacrylate as monomer. Normal ATRP, reverse ATRP, and AGET ATRP were all examined. The normal ATRP did not give a controlled system. AGET ATRP exhibited good performance, yielding PDI~1.3 with M_n ~30 k. Very small particle sizes (~40 nm) were obtained by using high Brij loading, [Brij 98]:[MMA] = 2.5:1. The ratio of [EBiB]:[Cu(II)] was 1:1 in the AGET experiments, signifying higher Cu(II) levels than used in the miniemulsion AGET experiments (1:04). Polystyrene latexes were also made (D_h ~38 nm), although the styrene polymerizations were slower than with methyl methacrylate.

The capability of making small particles via microemulsion was then further developed into a two-step emulsion polymerization process, thereby eliminating the need for a miniemulsion process [69]. While the miniemulsion process is robust and delivered good overall performance, it does require use of a high shear mixer and a costabilizer such as hexadecane. The first stage of the two-step process is an AGET microemulsion polymerization, giving a dispersion of small particles (~30–40 nm). This polymerization proceeds quickly (~10 min to ~30% conversion for *n*-butyl acrylate). There is no need to polymerize this stage to high conversion. The second stage involves swelling the microemulsion seed latex with additional monomer and continuing the polymerization. Particle diameters for *n*-butyl acrylate polymerizations grew from ~30–40 to ~90 nm during the second stage. Good control of the polymerization was observed, and the molecular weight distributions evolved without much evidence of a low molecular weight tail. Droplet formation is evidently not a problem in this process, which indicates there is no significant loss of the catalyst complex (including the BPMODA ligand) from the particle phase to the droplet phase, through either diffusion or collision.

The initial experiments utilized relatively high surfactant (Brij 98) concentrations, such that the final formulation contained ~75 wt% Brij 98 versus the monomer. However the authors were able to considerably reduce this level to 12 wt% versus monomer (3 wt% in the aqueous phase) by reducing the monomer content in the microemulsion step [69]. Using a more dilute system allowed them to also reduce the Brij 98 loading in the microemulsion. This change also required a decrease in the

CuBr₂/BPMODA level to ensure catalyst solubility in the monomer was maintained. A typical final formulation was as follows: [n-BA]:[EBiB]:[CuBr₂/BPMODA]:[ascorbic acid] = 300:1:0.15:0.22:0.06. A few points about this formulation are noteworthy in their difference from earlier miniemulsion formulations. The Cu(II) level is quite low at [EBiB]:[CuBr₂] = 1:0.15. Excess ligand is used ([CuBr₂]:[BPMODA] = 0.15:0.22) and the ascorbic level is only 40% of the Cu(II) loading, somewhat lower than in previous AGET experiments [68,72]. Arguably this is not an “ab initio” process in that the microemulsion step is essentially used to create a seed latex. However this is quite similar to how many industrial emulsion polymerization processes are conducted, with in situ formation of a dilute seed followed by monomer swelling and further polymerization.

3.5. Partitioning and compartmentalization in aqueous ATRP dispersions

The potential role of partitioning of the catalyst complex into the aqueous phase and its deleterious effects on the polymerization has been understood since the earliest studies from the Matyjaszewski laboratory, and it was this understanding that prompted them to develop more hydrophobic ligands [57]. Loss of Cu(I) and Cu(II) into the aqueous phase results in higher rates, loss of control, higher fractions of dead polymer and broader molecular weight distributions. Because the Cu(II) species are more soluble in the aqueous phase, the ratio of Cu(I):Cu(II) is also affected, with less Cu(II) being available at the reaction loci (particles). The Cu(I):Cu(II) ratio is more critical to maintaining control in ATRP than the absolute concentrations, and therefore alteration of this ratio by partitioning is undesirable. The role of partitioning and its possible effects were investigated using simulation and experiments for the styrene/CuBr/dNbpy system [73]. Reported results were consistent with previous experimental data, and it was further noted that Cu(II) partitioning led to higher rates only in the pre-stationary state, which can extend to hours in some systems. If a stationary state is achieved, Cu(II) partitioning was predicted to not affect the polymerization rate. Peng et al. also examined partitioning behavior using UV–VIS spectroscopy [74].

As discussed with SFRP, it has been generally believed that compartmentalization effects do

not exist in aqueous ATRP dispersions. Several studies have shown similar kinetics and molecular weight distributions for bulk and miniemulsion experiments run under the same or similar conditions [59,75]. Kagawa et al. [76] have conducted simulations to explore questions about possible compartmentalization and partitioning effects in dispersed ATRP for CuBr/dNbpy-mediated systems. They predicted compartmentalization effects may be evident for particle diameters <70 nm, resulting in lower polymerization rate but higher livingness.

3.6. Surfactant selection in emulsion-based ATRP

One of the major challenges facing emulsion-based ATRP is very limited range of suitable surfactants. Whereas most conventional emulsion polymerizations can be conducted with a wide range of surfactants, only a few have thus far proved suitable for ATRP. The most common surfactants used in emulsion polymerization, anionic surfactants with sulfate or sulfonate endgroups, are not compatible with ATRP catalysts. Several non-ionic surfactants have been evaluated [63,77] but only a couple of have been generally used. These are Brij 98 (polyoxyethylene(20) oleyl ether; used extensively by Matyjaszewski’s laboratory) and Tween 80 (polyoxyethylene sorbitan monooleate) [63,64,66,67]. The non-ionics are generally not as preferable as ionic surfactants, as they give larger particle sizes, less stable latexes, and become less effective at higher temperatures. Recently it was demonstrated that the cationic surfactant cetyltrimethylammonium bromide (CTAB) was an excellent stabilizer in the reverse ATRP of *n*-butyl methacrylate [78]. In comparison to non-ionics such as Brij 98, the CTAB can be used at low concentrations (1 wt% with respect to monomer) and at temperatures up to 90 °C, thereby enabling faster reaction rates, and yielding smaller particle sizes (~125–160 nm). Latexes were essentially coagulum free and displayed good shelf life stability.

For making larger particles, ATRP has also been reported in suspension [79,80]. Limer et al. [79] demonstrated that suspension polymerization of butyl methacrylate to give ~1–3 μm particles was viable with non-ionic and cationic surfactants, and with a variety of ligands. Both surfactant types were block copolymers made by L/CRP. The ionic surfactant was a PMMA-PDMAEMA (methyl

methacrylate-dimethylaminoethylmethacrylate) polymer with the PDMAEMA block quaternized. Larger beads (200–800 μm) of PMMA were obtained using poly(*N*-vinyl pyrrolidone) as a stabilizer [80].

3.7. Inverse miniemulsion ATRP

While most dispersed phase polymerizations are carried out in an aqueous continuous medium, there is a smaller but increasingly important demand for water-soluble polymers produced in particle form via inverse emulsion polymerization in which the continuous phase is oil-soluble. Inverse emulsions share many general features of an aqueous emulsion polymerization, and are well-suited to conduct polymerizations of water-soluble monomers, yielding a low viscosity dispersion that is easily handled and processed. Oh et al. [81,82] reported the polymerization of oligo(ethylene glycol) monomethyl ether methacrylate (OEOMA), beginning with a PEO macroinitiator, using an inverse miniemulsion in cyclohexane, based on AGET ATRP. The chain length of the macroinitiator was an important factor in determining colloidal stability, with shorter chains failing to give a stable dispersion. Crosslinking produced nanogels $\sim 200\text{--}300\text{ nm}$ in diameter. The nature of ATRP polymerization gives more uniform chain length in a linear polymer, and would be expected to give a more uniform network when crosslinked. Swelling ratios of the ATRP nanogel were 1.6–1.8 times higher than for a comparable conventional nanogel, bearing out this expectation. The nanogels could also be reduced to their linear chains, unlike conventionally polymerized gels.

3.8. Cobalt-mediated radical polymerization

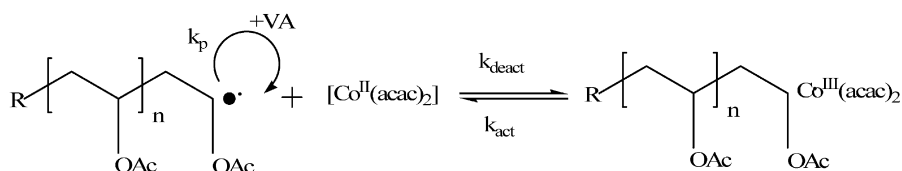
C/LRP has proven to be difficult for vinyl acetate polymerization, and only two prior publications examined vinyl acetate polymerization in dispersed systems (both miniemulsions using xanthates [83,84]). Cobalt-mediated polymerization of vinyl acetate using $\text{Co}(\text{acac})_2$ was recently reported in

bulk [85], suspension [86], and miniemulsion [87] (Scheme 11). A poly(vinyl acetate) macroinitiator terminated with $\text{Co}(\text{acac})_2$ was used in the suspension and miniemulsion processes to minimize loss of the relatively hydrophilic Co complex into the aqueous phase. The polymerizations proceed rapidly, even at 30 $^\circ\text{C}$, to yield $M_n \sim 80\text{ kg/mol}$ with conversions $> 90\%$. Polydispersities are comparable to those reported using xanthates for vinyl acetate polymerization in miniemulsion [83,84] but the cobalt-mediated polymerization gave somewhat higher rates and M_n . Interestingly, most of the conversion occurs during the ultrasonication step (6 min). The limits of the cobalt-mediated polymerization have not yet been fully explored and many questions remain about fundamental aspects of its nature, but its potential as a C/LRP process warrants further attention.

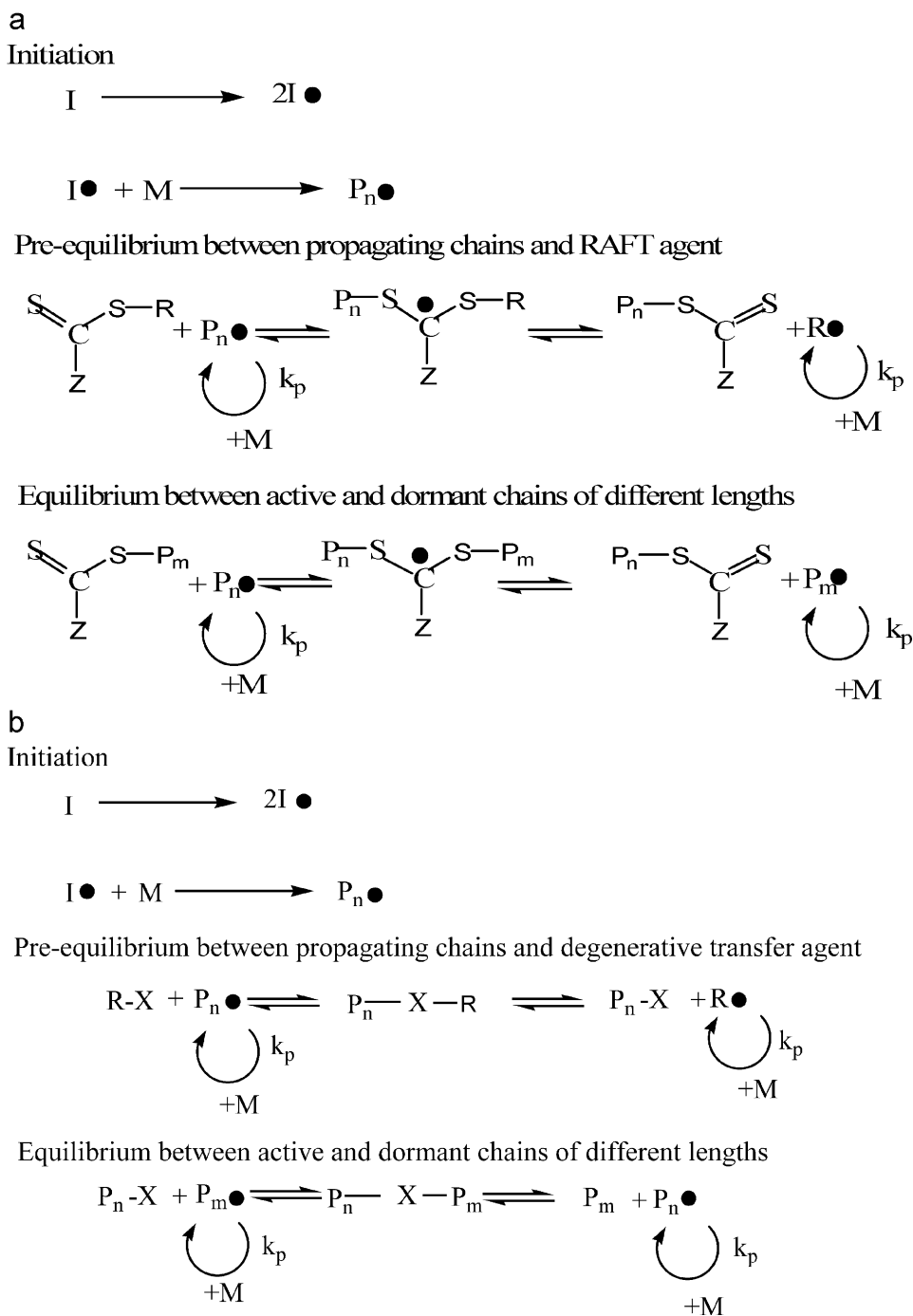
4. Reversible-addition–fragmentation–transfer (RAFT)

4.1. Overview

RAFT (Scheme 12(a)) and degenerative transfer (DT) (Scheme 12(b)) utilize a chain transfer agent that reacts with a propagating macroradical initiated by a conventional free radical initiator. The leaving group of the RAFT agent is a radical species which then initiates a chain. Scheme 13 shows some common RAFT agents used in (mini)emulsion studies. With DT, there is direct exchange, usually involving an iodine atom. The total number of chains in the system is the sum of transfer agent and primary radical molecules. A large excess of transfer agent to initiator yields higher livingness. A highly active transfer agent ($C_{tr} > \sim 100$) is rapidly consumed (within a few percent monomer conversion) while a less active transfer agent (e.g. xanthates; $C_{tr} \sim 1$) may take most of the polymerization to be consumed. Rapid consumption results in a narrower molecular weight distribution, while slow transfer agent consumption leads to a broader distribution. However the use of highly active



Scheme 11. Equilibrium between active and dormant chains in cobalt-mediated vinyl acetate polymerization [87].

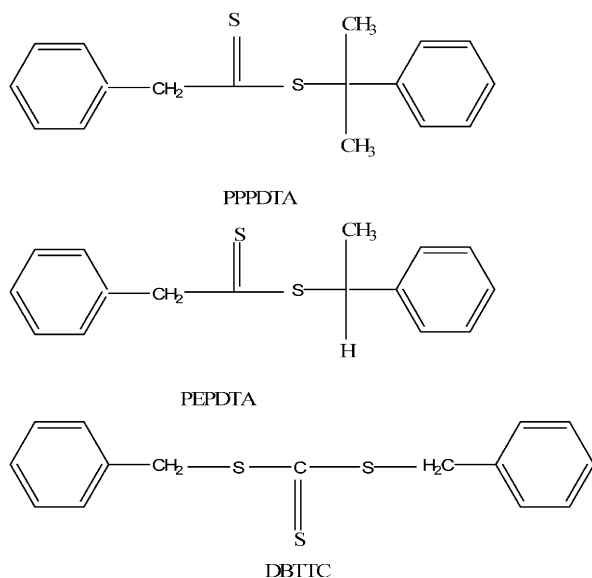


Scheme 12. Simplified reaction scheme for (a) RAFT; (b) Degenerative transfer

RAFT agents is also associated with formation of large oligomer concentrations at low conversions with subsequent formation of a monomer and RAFT agent rich surface layer, which is likely a result of superswelling [88]. The less active xanthates give broader MWDs but are much less likely to have

monomer layer formation, since the slow consumption of xanthate prevents high oligomer concentrations at low conversions.

Because a conventional initiator is used, new chains are continually being created as long as initiator remains. The average degree of polymerization is



Scheme 13. Structures of RAFT agents commonly used in (mini)emulsion.

given by

$$DP = \frac{[M]_0 - [M]}{([AB]_0 - [AB]) + \varepsilon([I]_0 - [I])}, \quad (6)$$

where $[AB]_0$ is the initial transfer agent concentration, $[AB]$ is concentration of transfer agent at any given time, $[I]_0$ is initial concentration of initiator, $[I]$ is initiator concentration at any given time and ε is initiator efficiency

As with SFRP, there is no simple, reliable equation for calculating polydispersity in RAFT systems; detailed simulations based on mathematical modeling are the best approach for predicting PDI [4]. RAFT can be used to polymerize a wide range of monomers and, like ATRP, does not require elevated temperatures. Rates in RAFT often exhibit retardation and/or inhibition effects, making predictive calculations unreliable.

4.2. RAFT in miniemulsion

As with SFRP and ATRP, RAFT polymerizations have generally proven to be more robust, better controlled and more colloidally stable when conducted in miniemulsion instead of emulsion. While considerable advances have occurred in emulsion, miniemulsion remains the more controllable process. Numerous papers have appeared in recent years reporting on various aspects of RAFT miniemulsions [89–108].

4.2.1. Kinetics and process development of RAFT miniemulsions

Perhaps the most important, and still not fully understood, factor in RAFT miniemulsions are the role(s) of the RAFT agent structure in determining kinetics, molecular weight distribution development and colloidal stability. Lansalot et al. [90] studied the role of RAFT agent structure on styrene miniemulsions, using three different RAFT agents; 1-phenylethyl phenyldithioacetate (PEPDTA), cumyl dithiobenzoate (CDB), and 1-phenylethyl dithiobenzoate (PEDB). Although in principle an ideal RAFT polymerization in (mini)emulsion should exhibit the same kinetics as the equivalent non-living system, the presence of the RAFT agent significantly slowed the rate for all three RAFT agents, even though the PEPDTA shows no retardation in bulk. Exit of the RAFT agent-leaving group to the aqueous phase was reported to be a driving factor in determining the overall rate. This conclusion was supported by an experiment using a macro-PEPDTA agent (for which no exit will occur) that showed no retardation compared to the conventional miniemulsion. A similar approach was used by Vosloo et al. [91] who prepared dithiobenzoate-terminated styrene oligomers in bulk, and then emulsified the mixture (with added hydrophobe) to create a stable miniemulsion. Phase separation in the form of a colored surface layer was not observed, and a controlled polymerization was obtained, although low M_n tailing was often seen. The length of the oligomers was potentially quite important, depending on the nature of the hydrophobe.

A detailed kinetic study that incorporated modified Smith-Ewart kinetics and included estimates of the RAFT equilibrium constant K_{eq} was published by Luo et al. [94]. Rate was found to be determined by both the K value and the RAFT agent concentration. Retardation was determined to be an inherent structural feature of RAFT miniemulsions (when zero-one kinetics are applicable) whose origin is different from retardation seen in bulk polymerization, and is attributable to the compartmentalized nature of the system. It is furthermore an effect separate from desorption of leaving group radicals. They also commented on the relative fragmentation rates of the intermediate radicals in concluding that fragmentation rate coefficients were high.

A series of papers dealing with process fundamentals of RAFT miniemulsions has been published

by researchers at Zhejiang University [92–96]. In the copolymerization of styrene and methyl methacrylate (MMA) mediated by 1-phenylethyl phenyl-dithioacetate (PEPDTA), it was found that the feed monomer composition plays an important role in the living nature of the polymerization [92]. While composition is not affected, the presence of different radicals at the chain ends can yield different kinetics depending on the relative concentrations of each radical type. When styrene was the predominant monomer, polymerizations were well controlled. However increasing the MMA fraction resulted in increasingly poor control. In a study designed to produce higher M_n polymers by altering process conditions and formulation, they achieved limited success [93]. While $M_n \sim 55$ kg/mol were produced in a batch process, poor control and increasing polydispersities with conversion also resulted. However when a semi-batch process was used, $M_n \sim 80$ kg/mol with PDI ~ 1.35 was obtained. The reason for this difference was not clear, but its root cause was believed to be different from similar results obtained by Smulders and Monteiro [109] who found that keeping the monomer concentration low (so that the number of monomer units added during each growth cycle is ~ 1) lowered the PDI.

The formation of large particles with a high concentration of oligomer, presumed to occur due to superswelling, and their deleterious effects on miniemulsion polymerizations were also investigated [95,96]. Increased levels of surfactant and/or costabilizer was shown to reduce PDI and give improved control and colloidal stability, and was attributed to suppression of the formation of these particles. The influence of a RAFT agent on the colloidal stability of styrene/hexadecane miniemulsions was investigated by Huang et al. [97] who came to a different conclusion than Luo et al. [1] concerning their “superswelling” hypothesis. They found upon careful examination of miniemulsions containing cumyl dithiobenzoate that two types of large droplets existed (much larger than the main miniemulsion population). One type is believed to result from Ostwald ripening and contained a lower than average RAFT agent concentration, while the second type which contains a high RAFT agent concentration is believed to result from coagulation of very small droplets. This latter type subsequently forms particles with low M_n polymer upon polymerization, some of which will form coagulum. While several experimental observations across numerous studies have been explained in terms of

“superswelling”, these new findings suggest re-examination of previous explanations is warranted, and it should be recognized that the issues involving colloidal stability in RAFT miniemulsions may be more complex than currently believed. Qi and Schork [110] further contributed to this question by studying the effect of RAFT agents on the diffusional stability of miniemulsions, prior to the occurrence of polymerization. Depending on the RAFT agent’s hydrophobicity, it may either improve or decrease the effectiveness of the miniemulsion costabilizer. This may in part explain why sometimes contradictory or inconsistent observations about colloidal stability in these systems have been reported.

The problem of transporting RAFT agent across the aqueous phase from droplets to particles to ensure homogeneous distribution of the RAFT agent across all particles was addressed through the use of β -cyclodextrin as a phase transfer agent in the polymerization of butyl methacrylate or styrene mediated by 2-cyanoprop-2-yl dithiobenzoate [98,99]. In the presence of the β -cyclodextrin, formation of the commonly observed monomer/oligomer surface layer was not observed (or was significantly reduced), coagulum formation was reduced and narrower molecular weight distributions were observed. A 1:1 (molar) ratio of RAFT agent to β -cyclodextrin yielded optimal results, although excess β -cyclodextrin appears to contribute to latex stability.

4.2.2. Structured and functional particles by RAFT miniemulsion

Research continues on using RAFT miniemulsions to prepare various particle and chain morphologies [100–106,111]. Carboxylated latexes, prepared using a RAFT agent containing a carboxylic acid group, were shown to have improved stability and reduced particle size [101]. Zeta potential and conductivity measurements suggest the acid group remains at least partially on or near the particle surface. Poly(4-acetoxystyrene)-*b*-polystyrene was made in bulk, solution and emulsion [111]. Subsequent hydrolysis of the acetoxy groups gave hydroxy polymers. Liquid-filled nanocapsules consisting of isooctane cores and polystyrene shells, where the shell was made using RAFT polymerization, were reported by Van Zyl et al. [102]. A wide variety of block copolymer structures, including diblocks and triblocks have been made using miniemulsion [92,103–106]. Design of a

suitable RAFT agent is often critical to success, with difunctional RAFT agents usually providing the most effective and flexible route to making multiple blocks. A process for nanoencapsulation using an “interfacially confined” RAFT miniemulsion polymerization has also been developed [100]. The principle is based on use of an amphiphilic RAFT agent that preferentially locates at the aqueous phase–particle interface during polymerization, thereby confining the polymerization loci to the particle surface. Amphiphilicity in the RAFT agent was obtained by making a styrene-maleic anhydride co-oligomer ($M_n \sim 1400$ g/mol) and then ammonolyzing the anhydride groups into carboxyls and amides. The procedure, which requires no additional surfactant, yielded mostly core-shell particles, although there was a minor population of pure polystyrene particles.

4.2.3. Xanthate-mediated polymerization of vinyl acetate in miniemulsion

Vinyl acetate has proven to be a difficult monomer to polymerize using L/CRP due to the high reactivity of the macroradical. Traditional RAFT agents such as dithioesters cannot polymerize vinyl acetate, possibly because of slow fragmentation due to the vinyl acetate macroradical being a poor leaving group. Using the xanthate methyl (ethoxycarbonothioyl)sulfanyl acetate (MESA) developed by Stenzel et al. [112], Russum et al. [84], and Simms et al. [83] polymerized vinyl acetate in miniemulsion with moderate success. The polymerization can be carried out using either oil-soluble [84] or water-soluble initiators [83], although better agreement between experimental and theoretical M_n 's were obtained with the oil-soluble initiator. At low conversions, control was excellent in these systems but deviations from linear kinetics and broadening molecular weight distributions were observed at higher conversions, possibly due to vinyl acetate's pronounced chain transfer to monomer and polymer.

4.2.4. RAFT inverse miniemulsion

Acrylamide was polymerized using 2-(2-carboxyethylsulfanylthiocarbonylsulfanyl) propionic acid in an inverse miniemulsion using cyclohexane as the continuous phase [113]. $MgSO_4$ was used as the costabilizer for the dispersed aqueous phase. The efficacy of both water-soluble (4,4'-azobis(4-cyanovaleic acid, ABCP)) and oil-soluble (azobisisobutyronitrile, AIBN) initiators was examined. Use of

AIBN resulted in poorly controlled polymerizations, while the ABCP yielded much better results. Even with the ABCP however, good control was evident only at low conversions. At conversions beyond $\sim 50\%$, loss of control was observed. This behavior, which was also seen in aqueous solution, was attributed to RAFT agent hydrolysis or aminolysis, may be largely preventable by buffering the aqueous phase pH to an appropriate value.

4.3. RAFT in emulsion

4.3.1. Seeded RAFT emulsion polymerization

Seeded RAFT emulsion processes have been studied either as an economically viable means to produce polymer with controlled microstructure, or as a tool to study particular kinetic features of RAFT polymerizations in emulsion. As previously described [1], early attempts at ab initio RAFT emulsion polymerization were beset by a number of problems, including poor control of the polymerization and coagulum formation, resulting from inadequate transport rates of the RAFT agent through the aqueous phase to the polymerizing particles. Use of seeded techniques (as well as the use of miniemulsions) has proven successful in overcoming many of the earlier difficulties. Prescott et al. [114] developed an acetone-assisted transport approach to facilitate diffusion of the RAFT agent to the particles in seeded styrene polymerizations. The seed particles were made by conventional (non-living) polymerization. To transport the RAFT agent (2-phenylprop-2-ylphenyldithioacetate, PPPDTA) to the seed particles, acetone was first added to the seed latex followed by addition of solid RAFT crystals. One to three days of stirring allowed the PPPDTA to be absorbed into the particles. Rotary evaporation was then used to remove the acetone. The technique yielded well-controlled polymerizations, although induction periods and rate retardation were observed as is common in RAFT (mini)emulsion systems. Szkurhan et al. [37] published details of a nanoprecipitation technique for RAFT polymerization of styrene, similar to an approach used with SFRP [36] and ATRP [38] and described earlier in this paper. Like Prescott et al., they used PPPDTA, but with their technique the seeds are also living. Control proved difficult to obtain with conventional initiators such as benzoyl peroxide or potassium persulfate, but autoinitiation at higher temperatures gave excellent control although rates were significantly

slower than in comparable TEMPO-mediated SFRP polymerizations.

Seeded polymerizations mediated by xanthates were used to make core-shell particles [109]. A non-living polymethylmethacrylate seed was used to fix the particle size distribution. The seed was then swollen with styrene and a xanthate (*O*-ethylxanthyl ethyl propionate) and polymerized to give the first block, followed by swelling with butyl acrylate which when polymerized yielded the second block. Although xanthates usually give high PDI because of their low reactivity, the authors found that slow monomer addition resulted in lower PDIs. This concept relies on the principle of keeping the monomer concentration low so that the number of monomer units added during each growth cycle is ~ 1 , ensuring that all chains grow at a fairly uniform rate.

The kinetic behavior of RAFT polymerizations in aqueous dispersions has proven to be even more complex than observed in bulk and solution, with the issues of transport of RAFT agent through the aqueous phase, RAFT agent partitioning into the aqueous phase, and possible exit of the leaving group from the particle all adding to the kinetic complexity. Seeded emulsion studies have provided a valuable tool for shedding light on some of these questions [115,116]. Smulders et al. [116] focused on low transfer constant (~ 0.7) xanthates in seeded styrene polymerizations using γ -radiolysis relaxation measurements to obtain exit rate coefficients. Entry rate coefficients were also determined from chemically initiated steady-state rate measurements. While the low transfer constant xanthates give broader molecular weight distributions (PDI ~ 2) than, for example dithioesters, they have proven useful in emulsion-based systems because their polymerizations do not exhibit an organic monomer-rich layer on the latex surface that that is common in many highly active RAFT emulsions. Exit of the xanthate-leaving group was believed to be responsible for the observed rate retardation. Increasing xanthate concentration leads to a higher exit rate coefficient and greater rate retardation. Surprisingly, the entry rate coefficient decreased in the presence of the xanthate, contrary to the existing theory that predicted the RAFT agent should not influence the entry rate. It was hypothesized that the xanthates are surface active (i.e. not uniformly distributed throughout the particle), and therefore there is an increased likelihood of entering oligoradicals transferring their activity to xanthates on or

near the particles surface. Given the propensity for the xanthate-leaving group to exit the particle, the overall effect is a net reduction in the entry rate.

Radical loss in seeded styrene polymerizations mediated by PPPDTA was explored by Prescott et al. [115]. Using the acetone transport technique described earlier with γ -radiolysis relaxation measurements, they found the radical loss rate to be strongly influenced by the presence of the PPPDTA. Experimental evidence suggested the presence of a “RAFT-induced exit mechanism” in which dormant oligomeric chains are formed by reaction between entering oligoradicals and RAFT agents in the particles. Since these entering radicals are thus prevented from propagating to longer chain lengths that are incapable of exit, there is effectively an increase in the radical exit rate as the oligoradicals can subsequently desorb from the particle surface. Radical entry therefore becomes a reversible process, with a significant enhancement of the radical desorption rate from particles ($\sim 400 \times$).

A more complete understanding of the RAFT kinetics enabled a Monte Carlo simulation study on how best to optimize the rate in RAFT emulsion polymerizations [117]. The modeling results also predicted that upon radical entry, rapid transfer to any RAFT agent present will likely occur resulting in formation of dormant oligomer. This phenomenon will enhance radical exit as the dormant oligomers fragment. Suggestions for minimizing rate retardation include use of less active transfer agents (the most beneficial), more hydrophobic R groups (to reduce inhibition) and lower diffusivity R groups to minimize termination.

A comprehensive kinetic model of seeded styrene emulsion polymerization based on population balance equations in both phases and accounting for compartmentalization offered insight into the causes of retardation and inhibition in seeded RAFT systems [118]. Experiments using cumyl dithiobenzoate were used to validate the model findings. Radical absorption/desorption and partitioning were also accounted for. Their findings were generally consistent with those of other investigations [115,117] in their explanations for the underlying causes of inhibition and retardation. Inhibition was found to result primarily from desorption of the RAFT leaving group, while retardation involved a combination of desorption of short radicals and increased termination due to the presence of non-surface anchored chains (derived from the RAFT agent-leaving group) that

can more readily diffuse inside particles and react with other radicals.

4.3.2. *Ab initio RAFT emulsion polymerization*

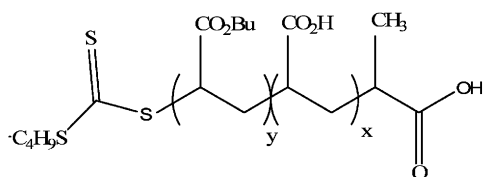
Two general approaches have been utilized in attempts to conduct *ab initio* emulsion polymerizations in RAFT: (1) a conventional approach (similar to a non-living *ab initio* emulsion) using RAFT agent with free radical initiators and stabilized by surfactant [119–123] and (2) a self-assembly approach in which living chains that are amphiphilic block copolymers act as both macroinitiators and stabilizing moieties [124–127].

Nozari and Tauer [119] conducted *ab initio* styrene polymerizations using three different initiators of varying water solubility, and four different RAFT agents with activating and leaving groups of varying solubility. Examination of the data shows a complex set of interactions between the initiator and RAFT agent solubility, affecting rate, particle size, molecular weight, and the degree of control over the polymerization. The extensive data set highlighted the difficulties in conducting *ab initio* RAFT emulsion polymerizations; control was often poor, evidenced by deviations from predicted M_n and high PDIs. For example, when using a (polyethylene glycol)-based macroinitiator that partitions into both phases, more hydrophilic RAFT agents lead to lower polymerization rates. However for the more water-soluble initiators potassium persulfate and 4,4'-azobis(4-cyanopentanoic acid), the opposite effect is observed, with more hydrophilic RAFT agents leading to higher polymerization rates. Further work led to the development of a technique to measure RAFT agent concentration in particles during polymerization [121]. Among the conclusions of this work are: (1) the diffusion rate of RAFT agents from monomer droplets to particles depends on the monomer solubility in water in addition to the RAFT agent hydrophilicity and (2) for styrene polymerizations the RAFT agent hydrophilicity corresponded to the degree of control. A somewhat surprising further conclusion from these studies was that sulfate radicals may directly enter particles, without first adding a few monomer units [120,121].

Factors influencing colloidal stability were the emphasis of a study by Luo and Cui [122] on *ab initio* methyl methacrylate polymerization mediated by 2-cyanoprop-2-yl dithiobenzoate. Using theoretical arguments based on the principle of “superswelling” (in which the presence of high oligomer

concentrations in particles at low conversions leads to excessive particle swelling), they predicted that colloidal stability would be better as initiation rates and theoretical M_n increased. Their experimental results appear to substantiate these claims. They further attributed the occurrence of poor M_n control and high PDIs to colloidal instability. They were able to achieve quite good results for *ab initio* RAFT emulsions by using high initiation rates and theoretical M_n , with good molecular weight control and minimal coagulum. Although they suggested their approach may also work with ATRP and SFRP, with SFRP excellent control may be maintained even if severe colloidal instability occurs (including coagulation). This implies the relationship between colloidal stability and control predicted by Luo and Cui for RAFT may not exist in other L/CRP systems. If compartmentalization is not important for SFRP and ATRP (or as important as in RAFT), this may offer an insight as to why with SFRP livingness can be achieved in the absence of colloidal stability, while in RAFT it cannot. Urbani et al. [123] postulated that the effects of superswelling were reduced in their PEPDTA-mediated styrene emulsion polymerizations because they achieved conditions of high particle nucleation rates and high radical entry rates, coupled with a high concentration of non-ionic surfactant (Brij 98). These conditions were realized by using fairly high [PEPDTA]:[styrene] ratios and a fixed ratio of PEPDTA to ammonium persulfate initiator. Solids loadings were either 10 or 20 wt%. Brij 98 concentration was 5 wt% in the aqueous phase. With this formulation, it was shown that most of the styrene was solubilized in micelles, which permitted fast transport of the PEPDTA to growing particles (faster than from large monomer droplets to particles). This procedure worked effectively provided M_n was <9k. Reduction of the [PEPDTA]:[styrene] to produce M_n >9k led to higher PDI, which was attributed to the increased role of superswelling as is commonly seen in RAFT systems with highly active RAFT agents such as PEPDTA.

The use of macroinitiators that function as both initiating species and stabilizing moieties provide superior control over an *ab initio* RAFT polymerization, although they are more complex. Gilbert has developed a self-assembly approach that uses micelle-forming amphiphilic block copolymers terminated with the desired RAFT agent (acrylic acid-*b*-butyl acrylate-RAFT) [124,125] (Scheme 14).



Scheme 14. Structure of amphiphilic block copolymer used in RAFT emulsion polymerization [124,125].

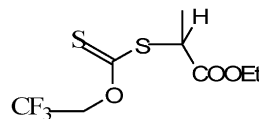
2-[[butylsulfanyl]-carbanothioyl]sulfanyl} propanoic acid and 2-[[dodecylsulfanyl]-carbanothioyl]sulfanyl}propanoic acid, which have low susceptibility to hydrolysis under acidic conditions, were employed as RAFT agents. The macro-RAFT agent effectively forms a seed, which can be swollen with monomer and grown as desired. Monomer droplets need to be prevented during formation of the seed latex, but this is readily achieved through carefully controlling the monomer feeding rate during synthesis of the second (hydrophobic) block of the macro-RAFT agent. (The presence of droplets containing RAFT agent can lead to appreciable droplet polymerization, which will likely negatively impact colloidal stability problems by leading to large polymer particles.) The RAFT agent is essentially “locked in” to the particles by this procedure, and is thereby prevented from partitioning into the aqueous phase, avoiding the difficulties encountered in conventional *ab initio* experiments [119–122]. Aggregation of the micelles occurs at low conversions, so that the final particle number is not equal to the initial micelle number. (A theoretical model was developed to enable prediction of particle number under different conditions [126].) An important consideration is that the monomers used in the preparation of the macro-RAFT agent must be able to propagate at a reasonable rate in the aqueous phase. Butyl acrylate has moderate water solubility and a very high propagation rate parameter, and is therefore a good candidate. Styrene, however, has limited water solubility and a much lower propagation rate parameter so that its propagation rate in the aqueous phase is too slow to be useful in this process. This limits the choice of suitable monomers for the macro-RAFT agent but does not restrict the choice of monomers used in the subsequent emulsion polymerization.

Surfactant-free styrene emulsion polymerization was carried out using a similar approach to that described above in which sodium acrylate (neutralized acrylic acid) was added as co-monomer [127]. Styrene-(sodium acrylate) random copolymers were

formed *in situ* and provided sufficient stabilization to give stable latexes with $D_n \sim 350\text{--}415$ nm (D_n , D_w are number, weight average particle diameters, respectively). The latexes had narrow particle size distributions ($D_w/D_n \sim 1.05\text{--}1.10$), a feature that can often be achieved with conventional surfactant-free processes. Final PDI approached 1.4 and the final M_n values were close to theoretically predicted values, although for most of the polymerization the actual M_n values are considerably larger than expected. This was believed to be related to slow consumption of the RAFT agent (dibenzylthiocarbonate), possibly due to slow transport through the aqueous phase.

Monteiro et al. [128] developed an *ab initio* emulsion process that avoided the use of self-assembly techniques. Recognizing the advantages of xanthates in emulsion-based systems, they synthesized a fluorinated xanthate (1-(*O*-trifluoroethylxanthyl)ethyl propionate) (Scheme 15) that has a transfer constant higher ($C_{tr} = 3.8$) than commonly used xanthates ($C_{tr} < \sim 1$). In *ab initio* styrene polymerizations, they were able to achieve reasonably narrow molecular weight distributions, with PDI decreasing from ~ 2 at low conversions to ~ 1.6 at full conversion. Furthermore, M_n values were predictable and reaction rates were acceptable. The improved performance of their xanthate appears to be due to a transfer constant value that is sufficiently low to prevent formation of the monomer layer but high enough to provide good control. Experimental data indicated transport of the fluorinated xanthate through the aqueous phase to particles was faster than its consumption inside the particles, so that its consumption was not diffusion controlled.

Poly(2-(diethylamino)ethyl methacrylate), made by RAFT using (4-cyanopentanoic acid)-4-dithiobenzoate, was used in the surfactant-free polymerization of styrene [129]. Addition of styrene units led to *in situ* formation of an amphiphilic block copolymer capable of stabilizing polymer particles. The objective of this work was not to control the emulsion polymerization step, but rather to



Scheme 15. The fluorinated xanthate (1-(*O*-trifluoroethylxanthyl)ethyl propionate) [128].

demonstrate the ability of the stabilizer generated in situ to yield a stable latex.

A different approach to surfactant-free RAFT emulsion polymerizations was demonstrated by Hartmann et al. [130] who studied the effects of degassing on the formation of an emulsion. In this process, repeated freeze–pump–thaw cycles lead to the formation of an emulsion, with a monomer layer on the liquid surface. There have been a few publications on this technique applied to emulsion polymerizations previously but this was the first application to L/CRP. It was shown that a controlled radical polymerization of styrene and a stable latex could be achieved using degassing, although many aspects of the behavior were not understood and will require further research to understand the real nature of the process.

4.4. RAFT microemulsion polymerization

Liu et al. polymerized *n*-hexyl methacrylate using 2-cyanoprop-2-yl dithiobenzoate to make 18–30 nm particles in a microemulsion process [131,132]. Satisfactory control of the polymerization was maintained provided the number of RAFT agent molecules exceeded the initial number of micelles. This restriction does somewhat limit the maximum achievable molecular weight as it imposes a joint restriction on the particle size and number of chains. Typical of microemulsions, the monomer loadings were low (~3 wt%) and the surfactant (dodecyltrimethylammonium bromide) loadings high (~12 wt%).

4.5. RAFT suspension polymerization

RAFT has been conducted in a suspension process [133], where poly(methylmethacrylate) beads (~160–550 μm in diameter) were made using 2-cyanoprop-2-yl dithiobenzoate. The bulk and suspension kinetics were observed to be similar, and good control/livingness was maintained over the polymerizations, as evidenced by low PDIs (~1.25) and successful chain extension experiments.

4.6. DT based on iodine exchange

4.6.1. DT using perfluoroalkyl iodide transfer agents

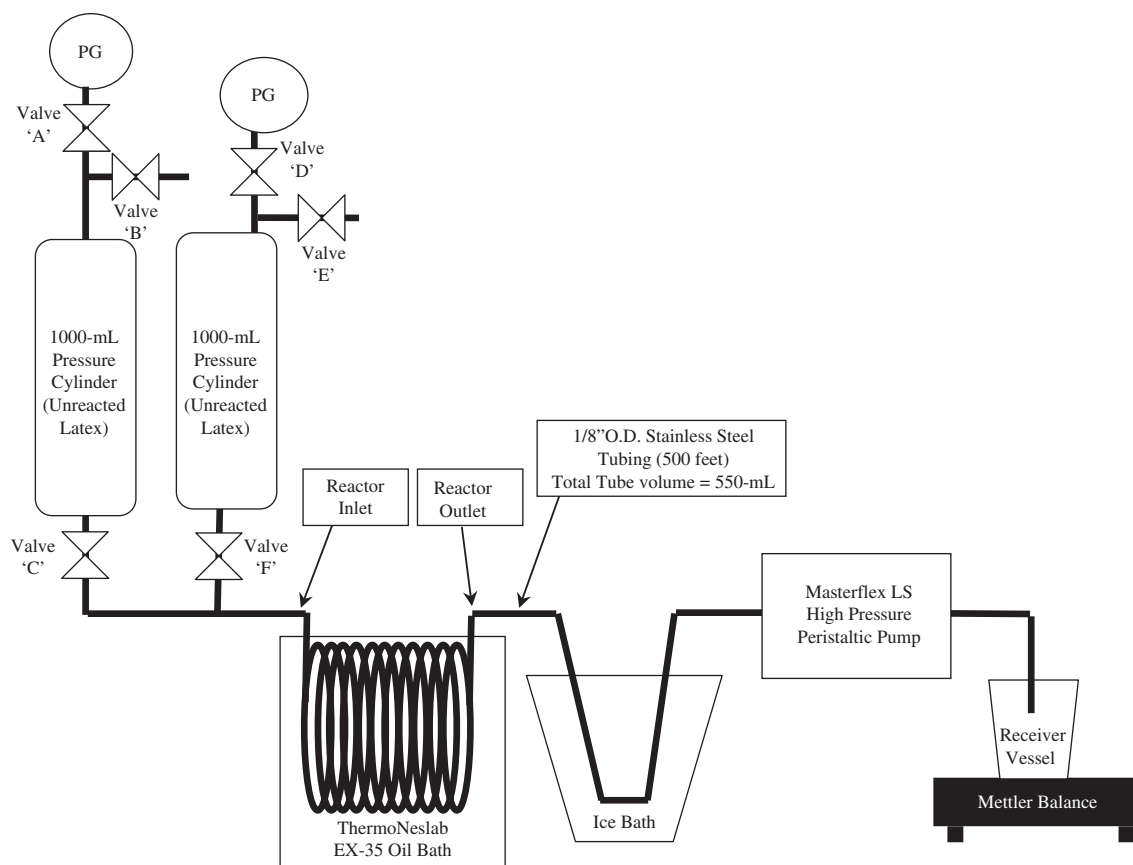
DT (Scheme 12(b)) based on the exchange of iodine using perfluorohexyl iodide has been previously reported in aqueous dispersed systems

[45,134,135]. Apostolo et al. [136] extended DT to microemulsion in the polymerization of the fluorinated monomers vinylidene fluoride and hexafluoropropylene, mediated by the transfer agent C₆F₁₂I₂. Lyons [137] reported the preparation of higher molecular weight fluoroelastomers (vinylidene fluoride–tetrafluoroethylene–hexafluoropropylene) in emulsion, initiated by ammonium persulfate and mediated by a perfluoroalkyl diiodide. Molecular weights were considerably higher than usually reported for L/CRP, with M_n varying from 100 k to 245 kg/mol and PDI~1.3. Quantification of the iodine content in the polymer chains verified that most chains retained their livingness.

Dispersion polymerization was used to make narrowly distributed micron-sized polystyrene particles in ethanol–water mixtures using either DT (perfluorohexyl iodide) or RAFT (1-cyano-1-methylpropyl dithiobenzoate) [138]. Critical to preserving a narrow particle size distribution was delaying the addition of the DT or RAFT agent until particle nucleation had occurred. Care also has to be exercised to ensure that the polymer molecular weight exceeds the critical molecular weight required for precipitation from the continuous phase, although this problem can be resolved by adjusting the continuous phase composition.

4.6.2. Reverse iodine transfer polymerization (RITP)

While in DT a perfluoroalkyl iodide compound is typically used as the transfer agent, in reverse iodine transfer Polymerization (RITP) elemental iodine is used as the mediating agent, and the transfer agent is generated in situ. Primary radicals arising from decomposition of a free radical initiator (or oligoradicals) react with I₂ to generate an adduct that functions as the transfer agent. (RITP and DT have an analogous relationship to Reverse ATRP and ATRP.) One mole of I₂ mediates two moles of chains. The process appears to have considerable versatility concerning monomer type, and has recently been adapted to ab initio emulsion polymerization of *n*-butyl acrylate [139] and miniemulsion polymerization of styrene [140]. Iodide is a powerful radical inhibitor, and readily reacts with any free radicals present in the reaction mixture. An inhibition period is therefore common in RITP, and lasts until all excess I₂ has been consumed. Iodine also hydrolytically disproportionates, resulting in reduction in the number of chains and upward deviation of M_n from its theoretical value.



Scheme 17. Schematic of tubular reactor used for TEMPO-mediated styrene miniemulsion polymerization [142].

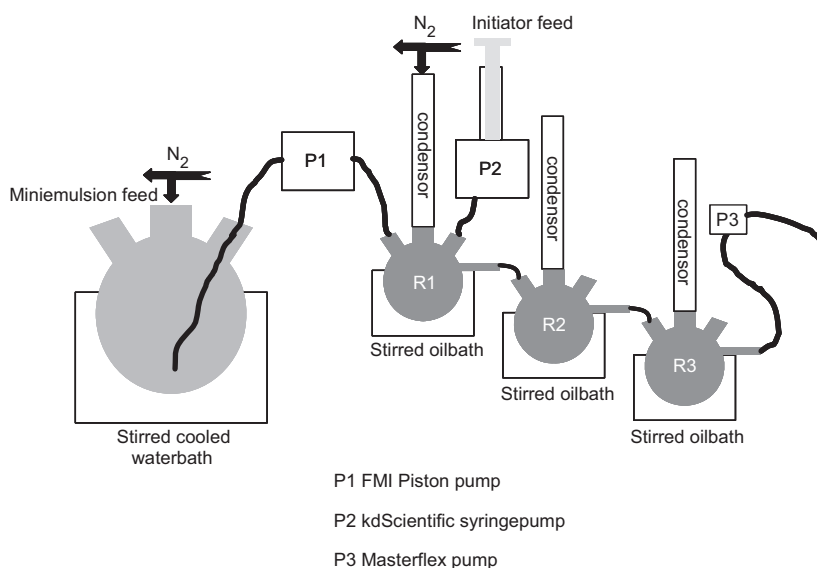
~3 h residence time. Chain extension of the polymerized latex indicated a high degree of livingness was preserved.

5.2. RAFT miniemulsions

Continuous miniemulsion RAFT processes have been investigated using a multi-tube reactor system [143–145] and a train of four stirred tanks in series ([146,147]. Using the RAFT agent 1-phenylethyl phenyldithioacetate (PEPDTA), styrene and butyl acrylate were polymerized in five different 1/16 in inner diameter perfluoroalkoxy tubes, with lengths ranging from 7.6 to 38.1 m. Kinetics in the tubes were compared to batch control experiments. While the rates were similar, there was a small but consistently higher rate observed in the tubes. Similarly, the PDIs in the tubes were consistently higher than in the comparable batch experiments. These differences were attributed to axial dispersion within the tubes. The role of residence time

distributions and flow regime were more extensively explored using tracer studies in which a hydrophobic dye was used to determine the residence time distribution of the miniemulsion droplet phase [143]. Although the Reynolds numbers used were quite low (< 10), laminar flow was not observed, contrary to expectation. This unusual behavior was attributed to fluid slippage at the tube wall. Axial dispersion was generally quite large, and believed to be responsible for the broader molecular weight distributions in the tubular reactor.

Continuous Stirred Tank Reactors (CSTRs) provide a quite different residence time environment for L/CRP. While tubular reactors may be expected to behave similarly to a batch tank reactor in that their residence time distributions are narrow, CSTRs have broad residence time distributions which are not conducive to achieving narrow molecular weight distributions in living systems. However, they do offer other advantages compared to other continuous reactor types, including ease



Scheme 18. Schematic of CSTR train used for RAFT miniemulsion polymerization. Reproduced with permission [147].

of making multi-block polymers, and the ability to make copolymers with a constant average composition within chains. In batch, semi-batch and tubular reactors, composition drift results from unequal reactivities of the respective monomers. In conventional radical polymerization, this leads to differences in average composition for chains made at different times during the process. In an L/CRP, the effect is somewhat different; there will be composition drift along the length of an individual chain. (The average composition of each chain will approximately be the same if all chains are initiated around the same time.) L/CRP in a CSTR eliminates this drift, albeit at the cost of broader molecular weight distributions. Smulders et al. [146,147] demonstrated that the RAFT agent PEPDTA can be used to produce styrene/butyl acrylate block copolymers with a high degree of chain end livingness in a train of four CSTRs, and that the process was quite flexible in allowing changes in polymer properties through changes in flow rate, injection point of the second monomer and temperature (Scheme 18).

6. Future perspectives

L/CRP has created a myriad of opportunities for synthesizing new macromolecular architectures, with potential applications in existing product markets as well as in emerging materials. Commercialization of L/CRP-based products will be facilitated by their

adaptation to heterogeneous systems because of the inherent economic advantages. Recent years have witnessed rapid expansion in interest, research activity and understanding in heterogeneous L/CRP, in SFRP, ATRP, and RAFT. The emergence of newer systems such as cobalt-mediated polymerizations and RITP and their immediate adaptation to aqueous systems underscore the increasing interest in this area. Despite the advances in our understanding of fundamental aspects of the chemistry of SFRP, ATRP, and RAFT as well as their behavior in dispersed aqueous systems, a number of challenges must still be addressed. Some of these issues are common to the different forms of L/CRP, while others are unique to each particular system.

Problems common to SFRP, ATRP, and RAFT include the presence of a residual-mediating agent in the product and added process complexity (and therefore cost) compared to conventional radical polymerizations. The nature of the mediating agent and the product application are critical in determining the acceptable residual concentrations in a final product. RAFT and SFRP require one nitroxide or RAFT agent per chain, while in ATRP one catalyst molecule can effectively mediate the growth of several chains. The presence of residual-mediating agent raises concerns about color, odor, stability, and environmental legislative compliance. Removal of mediating agents from aqueous dispersions is likely to be more difficult than from homogeneous

solutions. These issues will need to be addressed to successfully commercialize a product using L/CRP.

Increased process complexity compared to conventional emulsion-based systems is another concern for L/CRP, although there is usually increased cost tolerance because of the higher valued-added nature of the product. As described throughout this review, significant progress has been achieved in the past few years in advancing our L/CRP process understanding, and in the development of procedures that addressed prior challenges. However, there has been relatively little effort to-date on the reaction engineering aspects of heterogeneous L/CRP, and this is an area that will require further research and development as processes approach commercialization.

Most research on L/CRP in aqueous dispersed systems has centered on adapting solution or bulk processes to a heterogeneous environment, and addressing the numerous challenges that have arisen. With many of these issues at least partially resolved, more attention can now turn to exploiting the potential advantages of conducting a polymerization in a reactor with nanosize dimensions. As it was developed and studied, conventional emulsion polymerization proved capable of enabling polymer properties and morphologies that could not be realized in bulk or solution polymerization. As we better comprehend the nature of heterogeneous L/CRP, similar new opportunities should emerge. Simms [55] demonstration that molecular weights $\sim 1,000,000$ g/mol can be made by ATRP in miniemulsion, while such high molecular weights are not achievable in bulk, is an illustration of a heterogeneous system enabling otherwise unattainable properties. Future research in heterogeneous L/CRP is poised to discover other microstructural and morphological properties that are uniquely enabled by confining reactions to nanosize dimensions.

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References

- [1] Cunningham MF. Living/controlled radical polymerizations in dispersed phase systems. *Prog Polym Sci* 2002;27: 1039–67.
- [2] Qiu J, Charleux B, Matyjaszewski K. Controlled/living radical polymerization in aqueous media: homogeneous and heterogeneous systems. *Prog Polym Sci* 2001;26: 2083–134.
- [3] Braunecker WA, Matyjaszewski K. Controlled/living radical polymerization: features, developments, and perspectives. *Prog Polym Sci* 2007;32:93–146.
- [4] Monteiro MJ. Design strategies for controlling the molecular weight and rate using reversible addition–fragmentation chain transfer mediated living radical polymerization. *J Polym Sci Part A: Polym Chem* 2005;43: 3189–204.
- [5] Shipp DA. Living radical polymerization: controlling molecular size and chemical functionality in vinyl polymers. *J Macromol Sci Polym Rev* 2005;C45:171–94.
- [6] Kamigaito M, Ando T, Sawamoto M. Metal-catalyzed living radical polymerization: discovery and developments. *Chem Rec* 2004;4:159–75.
- [7] Goto A, Fukuda T. Kinetics of living radical polymerization. *Prog Polym Sci* 2004;29:329–85.
- [8] Limer A, Haddleton DM. Transition metal mediated living radical polymerisation. *Prog React Kinet Mech* 2004;29: 187–241.
- [9] Save M, Guillaenuef Y, Gilbert RG. Controlled radical polymerization in aqueous dispersed media. *Aust J Chem* 2006;59:693–711.
- [10] Monteiro MJ, Charleux B. Living radical polymerisation in emulsion and miniemulsion. *Chem Technol Emuls Polymerisat* 2005:111–39.
- [11] Cunningham MF. Recent Progress in Nitroxide Mediated Polymerization in Miniemulsions. *CR Chim* 2004;6: 1351–74.
- [12] Reimers J, Schork FJ. Robust nucleation in polymer-stabilized miniemulsion polymerization. *J Appl Polym Sci* 1996;59:1833–41.
- [13] Lovell PA, El-Aasser MS. *Emulsion polymerization and emulsion polymers*. New York: Wiley; 1997.
- [14] Ma JW, Smith JA, McAuley KB, Cunningham MF, Keoshkerian B, Georges MK. Nitroxide-mediated radical polymerization of styrene in miniemulsion: model studies of alkoxyamine-initiated systems. *Chem Eng Sci* 2003;58: 1163–76.
- [15] Ma JW, Cunningham MF, McAuley KB, Keoshkerian B, Georges M. Nitroxide mediated living radical polymerization of styrene in miniemulsion-modelling persulfate-initiated systems. *Chem Eng Sci* 2003;58:1177–90.
- [16] Ma JW, Cunningham MF, McAuley KB, Keoshkerian B, Georges MK. Model studies of nitroxide-mediated styrene miniemulsion polymerization—opportunities for process improvement. *Macromol Theory Simul* 2003;12:72–85.
- [17] Ma JW, Cunningham MF, McAuley KB, Keoshkerian B, Georges MK. Interfacial mass transfer in nitroxide-mediated miniemulsion polymerization. *Macromol Theory Simul* 2002;11:953–60.
- [18] Tortosa K, Smith J, Cunningham MF. Synthesis of polystyrene-block-poly(butyl acrylate) copolymers using

- nitroxide-mediated living radical polymerization in miniemulsion. *Macromol Rapid Commun* 2001;22:957–61.
- [19] Zetterlund PB, Okubo M. Nitroxide-mediated radical polymerization in miniemulsion at stationary state: rationale for independence of polymerization rate on nitroxide partitioning using oil-phase initiation. *Macromol Theory Simul* 2005;14:415–20.
- [20] Lin M, Hsu JCC, Cunningham MF. Role of sodium dodecylbenzenesulfonate in 2,2,6,6-tetramethyl-1-piperidinyloxy-mediated styrene miniemulsion polymerization. *J Polym Sci Part A: Polym Chem* 2006;44:5974–86.
- [21] Cunningham M, Lin M, Smith J, Ma J, McAuley K, Keoshkerian B, et al. Nitroxide-mediated living radical polymerization in dispersed systems. *Prog Colloid Polym Sci* 2004;124:88–93.
- [22] Osti M, Cunningham MF, Whitney R, Keoshkerian B. Miniemulsion polymerization initiated by L-ascorbic acid and sulfonate/sulfate surfactants. *J Polym Sci Part A: Polym Chem* 2006;45:69–80.
- [23] Pan G, Sudol ED, Dimonie VL, El-Aasser MS. Surfactant concentration effects on nitroxide-mediated living free radical miniemulsion polymerization of styrene. *Macromolecules* 2002;35:6915–9.
- [24] Cunningham MF, Tortosa K, Lin M, Keoshkerian B, Georges MK. Influence of camphorsulfonic acid in nitroxide-mediated styrene miniemulsion polymerization. *J Polym Sci Part A: Polym Chem* 2002;40:2828–41.
- [25] Fischer H. The persistent radical effect: a principle for selective radical reactions and living radical polymerizations. *Chem Rev* 2001;101:3581–610.
- [26] Cunningham M, Lin M, Buragina C, Milton S, Ng D, Hsu CC, et al. Maximizing polymer livingness in nitroxide-mediated miniemulsion polymerizations. *Polymer* 2005;46:1025–32.
- [27] Lin M, Cunningham MF, Keoshkerian B. Achieving high conversions in nitroxide-mediated living styrene miniemulsion polymerization. *Macromol Symp* 2004;206:263–74.
- [28] Cunningham MF, Ng DCT, Milton SG, Keoshkerian B. Low temperature TEMPO-mediated styrene polymerization in miniemulsion. *J Polym Sci Part A: Polym Chem* 2006;44:232–42.
- [29] Scott ME, Parent JS, Hennigar SL, Whitney RA, Cunningham MF. Determination of alkoxyamine concentrations in nitroxyl-mediated styrene polymerization products. *Macromolecules* 2002;35:7628–33.
- [30] Nur Alam M, Zetterlund PB, Okubo M. Network formation in nitroxide-mediated radical copolymerization of styrene and divinylbenzene in miniemulsion. *Macromol Chem Phys* 2006;207:1732–41.
- [31] Saka Y, Zetterlund PB, Okubo M. Gel formation and primary chain lengths in nitroxide-mediated radical copolymerization of styrene and divinylbenzene in miniemulsion. *Polymer* 2007;48:1229–36.
- [32] Zetterlund PB, Alam MN, Minami H, Okubo M. Nitroxide-mediated controlled/living free radical copolymerization of styrene and divinylbenzene in aqueous miniemulsion. *Macromol Rapid Commun* 2005;26:955–60.
- [33] Keoshkerian B, MacLeod PJ, Georges MK. Block copolymer synthesis by a miniemulsion stable free radical polymerization process. *Macromolecules* 2001;34:3594–9.
- [34] Georges MK, Lukkarila JL, Szkurhan AR. TEMPO-mediated *n*-butyl acrylate polymerizations. *Macromolecules* 2004;37:1297–303.
- [35] Keoshkerian B, Szkurhan AR, Georges MK. Nitroxide-mediated miniemulsion acrylate polymerization. *Macromolecules* 2001;34:6531–2.
- [36] Szkurhan A, Georges MK. Stable free-radical emulsion polymerization. *Macromolecules* 2004;37:4776–82.
- [37] Szkurhan AR, Kasahara T, Georges MK. Reversible-addition fragmentation chain transfer radical emulsion polymerization by a nanoprecipitation process. *J Polym Sci Part A: Polym Chem* 2006;44:5708–18.
- [38] Chan-Seng D, Georges MK. Living radical emulsion polymerization using the nanoprecipitation technique: an extension to atom transfer radical polymerization. *J Polym Sci Part A: Polym Chem* 2006;44:4027–38.
- [39] Farcet C, Nicolas J, Charleux B. Kinetic study of the nitroxide-mediated controlled free-radical polymerization of *n*-butyl acrylate in aqueous miniemulsions. *J Polym Sci Part A: Polym Chem* 2002;40:4410–20.
- [40] Nicolas J, Charleux B, Guerret O, Magnet S. Novel SG1-based water-soluble alkoxyamine for nitroxide-mediated controlled free-radical polymerization of styrene and *n*-butyl acrylate in miniemulsion. *Macromolecules* 2004;37:4453–63.
- [41] Nicolas J, Charleux B, Guerret O, Magnet S. Nitroxide-mediated controlled free-radical emulsion polymerization of styrene and *n*-butyl acrylate with a water-soluble alkoxyamine as initiator. *Angew Chem Int Ed* 2004;43:6186–9.
- [42] Delaittre G, Nicolas J, Lefay C, Save M, Charleux B. Surfactant-free synthesis of amphiphilic diblock copolymer nanoparticles *via* nitroxide-mediated emulsion polymerization. *Chem Commun* 2005;2005:614–6.
- [43] Nicolas J, Charleux B, Guerret O, Magnet S. Nitroxide-mediated controlled free-radical emulsion polymerization using a difunctional water-soluble alkoxyamine initiator, toward the control of particle size, particle size distribution, and the synthesis of triblock copolymers. *Macromolecules* 2005;38:9963–73.
- [44] Nicolas J, Charleux B, Magnet S. Multistep and semibatch nitroxide-mediated controlled free-radical emulsion polymerization: A significant step toward conceivable industrial processes. *J Polym Sci Part A: Polym Chem* 2006;44:4142–53.
- [45] Butte A, Storti G, Morbidelli M. Miniemulsion living free radical polymerization of styrene. *Macromolecules* 2000;33:3485–7.
- [46] Pan G, Sudol ED, Dimonie VL, El-Aasser MS. Nitroxide-mediated living free radical miniemulsion polymerization of styrene. *Macromolecules* 2001;34:481–8.
- [47] Cunningham MF, Xie M, McAuley KB, Keoshkerian B, Georges MK. Nitroxide-mediated styrene miniemulsion polymerization. *Macromolecules* 2002;35:59–66.
- [48] Pan G, Sudol ED, Dimonie VL, El-Aasser MS. Thermal self-initiation of styrene in the presence of TEMPO radicals: bulk and miniemulsion. *J Polym Sci Part A: Polym Chem* 2004;42:4921–32.
- [49] Nakamura T, Zetterlund PB, Okubo M. Particle size effects in TEMPO-mediated radical polymerization of styrene in aqueous miniemulsion. *Macromol Rapid Commun* 2006;27:2014–8.

- [50] Charleux B. Theoretical aspects of controlled radical polymerization in a dispersed medium. *Macromolecules* 2000;33:5358–65.
- [51] Butte A, Storti M, Morbidelli M. Pseudo-living polymerization of styrene in miniemulsion. *DECHEMA Monogr* 1998;134:497–507.
- [52] Zetterlund PB, Okubo M. Compartmentalization in nitroxide-mediated radical polymerization in dispersed systems. *Macromolecules* 2006;39:8959–67.
- [53] Maehata H, Buragina C, Keoshkerian B, Cunningham MF. Compartmentalization in TEMPO-mediated styrene miniemulsion polymerization. *Macromolecules* 2007;40:7126–31.
- [54] Min K, Jakubowski W, Matyjaszewski K. AGET ATRP in the presence of air in miniemulsion and in bulk. *Macromol Rapid Commun* 2006;27:594–8.
- [55] Simms RW, Cunningham MF. High molecular weight poly(butyl methacrylate) by reverse atom transfer radical polymerization in miniemulsion initiated by a redox System. *Macromolecules* 2007;40:860–6.
- [56] Quemener D, Bousquet A, Heroguez V, Gnanou Y. Hybrid polymer particles by tandem ring-opening metathesis and atom transfer radical polymerizations in aqueous miniemulsion. *Macromolecules* 2006;39:5589–91.
- [57] Li M, Matyjaszewski K. Further progress in atom transfer radical polymerizations conducted in a waterborne system. *J Polym Sci Part A: Polym Chem* 2003;41:3606–14.
- [58] Li M, Matyjaszewski K. Reverse atom transfer radical polymerization in miniemulsion. *Macromolecules* 2003;36:6028–35.
- [59] Li M, Min K, Matyjaszewski K. ATRP in waterborne miniemulsion via a simultaneous reverse and normal initiation process. *Macromolecules* 2004;37:2106–12.
- [60] Li M, Jahed NM, Min K, Matyjaszewski K. Preparation of linear and star-shaped block copolymers by ATRP using simultaneous reverse and normal initiation process in bulk and miniemulsion. *Macromolecules* 2004;37:2434–41.
- [61] Min KE, Li M, Matyjaszewski K. Preparation of gradient copolymers via ATRP using a simultaneous reverse and normal initiation process, I, spontaneous gradient. *J Polym Sci Part A: Polym Chem* 2005;43:3616–22.
- [62] Min K, Gao H, Matyjaszewski K. Preparation of homopolymers and block copolymers in miniemulsion by ATRP using activators generated by electron transfer (AGET). *J Am Chem Soc* 2005;127:3825–30.
- [63] Eslami H, Zhu S. Emulsion atom transfer radical polymerization of 2-ethylhexyl methacrylate. *Polymer* 2005;46:5484–93.
- [64] Eslami H, Zhu S. Emulsion atom transfer radical block copolymerization of 2-ethylhexyl methacrylate and methyl methacrylate. *J Polym Sci Part A: Polym Chem* 2006;44:1914–25.
- [65] Peng H, Cheng S, Feng L. Properties of poly(*n*-butyl methacrylate) prepared by reverse atom transfer radical polymerization in an aqueous dispersed system. *J Appl Polym Sci* 2003;89:1542–7.
- [66] Okubo M, Minami H, Zhou J. Preparation of block copolymer by atom transfer radical seeded emulsion polymerization. *Colloid Polym Sci* 2004;282:747–52.
- [67] Kagawa Y, Minami H, Okubo M, Zhou J. Preparation of block copolymer particles by two-step atom transfer radical polymerization in aqueous media and its unique morphology. *Polymer* 2005;46:1045–9.
- [68] Min K, Matyjaszewski K. Atom transfer radical polymerization in microemulsion. *Macromolecules* 2005;38:8131–4.
- [69] Min K, Gao H, Matyjaszewski K. Development of an ab initio emulsion atom transfer radical polymerization: from microemulsion to emulsion. *J Am Chem Soc* 2006;128:10521–6.
- [70] Capek I. Microemulsion polymerization of styrene in the presence of anionic emulsifier. *Adv Colloid Interface Sci* 1999;82:253–73.
- [71] Capek I. Microemulsion polymerization of styrene in the presence of a cationic emulsifier. *Adv Colloid Interface Sci* 2001;92:195–233.
- [72] Smith W, Vez J. Kinetics of emulsion polymerization. *J Chem Phys* 1948;16:592–9.
- [73] Kagawa Y, Zetterlund PB, Minami H, Okubo M. Atom transfer radical polymerization in miniemulsion: partitioning effects of copper(I) and copper(II) on polymerization rate, livingness, and molecular weight distribution. *Macromolecules* 2007;40:3062–9.
- [74] Peng H, Cheng S, Feng L, Fan Z. Atom transfer radical polymerization of *n*-butyl methacrylate in an aqueous dispersed system. *J Appl Polym Sci* 2003;89:3175–9.
- [75] Matyjaszewski K, Qiu J, Tsarevsky NV, Charleux B. Atom transfer radical polymerization of *n*-butyl methacrylate in an aqueous dispersed system: a miniemulsion approach. *J Polym Sci Part A: Polym Chem* 2000;38:4724–34.
- [76] Kagawa Y, Zetterlund PB, Minami H, Okubo M. Compartmentalization in atom transfer radical polymerization in dispersed systems. *Macromol Theory Simul* 2006;15:608–13.
- [77] Gaynor SG, Qiu J, Matyjaszewski K. Controlled/“living” radical polymerization applied to water-borne systems. *Macromolecules* 1998;31:5951–4.
- [78] Simms RW, Cunningham MF. Reverse atom transfer radical polymerization of butyl methacrylate in a miniemulsion stabilized with a cationic surfactant. *J Polym Sci Part A: Polym Chem* 2006;44:1628–34.
- [79] Limer A, Heming A, Shirley I, Haddleton D. Living radical polymerization in heterogeneous conditions-suspension polymerization. *Eur Polym J* 2005;41:805–16.
- [80] Bicak N, Gazi M, Tunca U, Kucukkaya I. Utility of atom transfer radical polymerization for the preparation of poly(methyl methacrylate) beads in an aqueous suspension. *J Polym Sci Part A: Polym Chem* 2004;42:1362–6.
- [81] Oh JK, Perineau F, Matyjaszewski K. Preparation of nanoparticles of well-controlled water-soluble homopolymers and block copolymers using an inverse miniemulsion ATRP. *Macromolecules* 2006;39:8003–10.
- [82] Oh JK, Tang C, Gao H, Tsarevsky NV, Matyjaszewski K. Inverse miniemulsion ATRP: a new method for synthesis and functionalization of well-defined water-soluble/cross-linked polymeric particles. *J Am Chem Soc* 2006;128:5578–84.
- [83] Simms RW, Davis TP, Cunningham MF. Xanthate-mediated living radical polymerization of vinyl acetate in miniemulsion. *Macromol Rapid Commun* 2005;26:592–6.
- [84] Russum JP, Barbre ND, Jones CW, Schork FJ. Miniemulsion reversible addition fragmentation chain transfer polymerization of vinyl acetate. *J Polym Sci Part A: Polym Chem* 2005;43:2188–93.

- [85] Debuigne A, Caille J, Jerome R. Highly efficient cobalt-mediated radical polymerization of vinyl acetate. *Angew Chem Int Ed* 2005;44:1101–4.
- [86] Debuigne A, Caille J, Detrembleur C, Jerome R. Effective cobalt mediation of the radical polymerization of vinyl acetate in suspension. *Angew Chem Int Ed* 2005;44:3439–42.
- [87] Detrembleur C, Debuigne A, Bryaskova R, Charleux B, Jerome R. Cobalt-mediated radical polymerization of vinyl acetate in miniemulsion: very fast formation of stable poly(vinyl acetate) latexes at low temperature. *Macromol Rapid Commun* 2006;27:37–41.
- [88] Luo Y, Tsavalas J, Schork FJ. Theoretical aspects of particle swelling in living free radical miniemulsion polymerization. *Macromolecules* 2001;34:5501–7.
- [89] de Brouwer H, Tsavalas JG, Schork FJ, Monteiro MJ. Living radical polymerization in miniemulsion using reversible addition–fragmentation chain transfer. *Macromolecules* 2000;33:9239–46.
- [90] Lansalot M, Davis TP, Heuts JPA. RAFT miniemulsion polymerization: influence of the structure of the RAFT agent. *Macromolecules* 2002;35:7582–91.
- [91] Vosloo JJ, De Wet-Roos D, Tonge MP, Sanderson RD. Controlled free radical polymerization in water-borne dispersion using reversible addition–fragmentation chain transfer. *Macromolecules* 2002;35:4894–902.
- [92] Luo Y, Liu X. Reversible addition–fragmentation transfer (RAFT) copolymerization of methyl methacrylate and styrene in miniemulsion. *J Polym Sci Part A: Polym Chem* 2004;42:6248–58.
- [93] Yang L, Luo Y, Li B. RAFT miniemulsion polymerization targeting to polymer of higher molecular weight. *J Polym Sci Part A: Polym Chem* 2005;43:4972–9.
- [94] Luo Y, Wang R, Yang L, Yu B, Li B, Zhu S. Effect of reversible addition–fragmentation transfer (RAFT) reactions on (mini)emulsion polymerization kinetics and estimate of RAFT equilibrium constants. *Macromolecules* 2006;39:1328–37.
- [95] Yang L, Luo Y, Li B. Reversible addition fragmentation transfer (RAFT) polymerization of styrene in a miniemulsion: a mechanistic investigation. *Polymer* 2006;47:751–62.
- [96] Yang L, Luo Y, Li B. The influence of surfactant coverage of the minidroplets on RAFT miniemulsion polymerization. *J Polym Sci Part A: Polym Chem* 2006;44:2293–306.
- [97] Huang X, Sudol ED, Dimonie VL, Anderson CD, El-Aasser MS. Stability in styrene/HD miniemulsions containing a RAFT agent. *Macromolecules* 2006;39:6944–50.
- [98] Yu Z, Ji X, Ni P. Living radical miniemulsion polymerization by RAFT in the presence of beta-cyclodextrin. *Colloid Polym Sci* 2006;285:211–8.
- [99] Zhang F, Ni P, Xiong Q, Yu Z. Reversible addition–fragmentation chain transfer/miniemulsion polymerization of butyl methacrylate in the presence of *b*-cyclodextrin. *J Polym Sci Part A: Polym Chem* 2005;43:2931–40.
- [100] Luo Y, Gu H. A general strategy for nano-encapsulation via interfacially confined living/controlled radical miniemulsion polymerization. *Macromol Rapid Commun* 2006;27:21–5.
- [101] Shim SE, Lee H, Choe S. Synthesis of functionalized monodisperse poly(methyl methacrylate) nanoparticles by a RAFT agent carrying carboxyl end group. *Macromolecules* 2004;37:5565–71.
- [102] Van Zyl AJP, Bosch RFP, McLeary JB, Sanderson RD, Klumperman B. Synthesis of styrene based liquid-filled polymeric nanocapsules by the use of RAFT-mediated polymerization in miniemulsion. *Polymer* 2005;46:3607–15.
- [103] Bowes A, Mcleary JB, Sanderson RD. AB and ABA type butyl acrylate and styrene block copolymers via RAFT-mediated miniemulsion polymerization. *J Polym Sci Part A: Polym Chem* 2007;45:588–604.
- [104] Bussels R, Bergman-Goettgens C, Meuldijk J, Koning C. Multiblock copolymers synthesized by miniemulsion polymerization using multifunctional RAFT agents. *Macromolecules* 2004;37:9299–301.
- [105] Bussels R, Bergman-Goettgens C, Meuldijk J, Koning C. Multiblock copolymers synthesized in aqueous dispersions using multifunctional RAFT agents. *Polymer* 2005;46:8546–54.
- [106] Zhou X, Ni P, Yu Z, Zhang F. Latices of poly(fluoroalkyl methacrylate)-*b*-poly(butyl methacrylate) copolymers prepared via reversible addition–fragmentation chain transfer polymerization. *J Polym Sci Part A: Polym Chem* 2006;45:471–84.
- [107] Mcleary JB, Tonge MP, De Wet Roos D, Sanderson RD, Klumperman B. Controlled, radical reversible addition–fragmentation chain-transfer polymerization in high-surfactant-concentration ionic miniemulsions. *J Polym Sci Part A: Polym Chem* 2004;42:960–74.
- [108] Matahwa H, McLeary JB, Sanderson RD. Comparative study of classical surfactants and polymerizable surfactants (surfmers) in the reversible addition–fragmentation chain transfer mediated miniemulsion polymerization of styrene and methyl methacrylate. *J Polym Sci Part A: Polym Chem* 2005;44:427–42.
- [109] Smulders W, Monteiro MJ. Seeded emulsion polymerization of block copolymer core-shell nanoparticles with controlled particle size and molecular weight distribution using xanthate-based RAFT polymerization. *Macromolecules* 2004;37:4474–83.
- [110] Qi G, Schork FJ. On the stability of miniemulsions in the presence of RAFT agents. *Langmuir* 2006;22:9075–8.
- [111] Kanagasabapathy S, Sudalai A, Benicewicz BC. Reversible addition–fragmentation chain-transfer polymerization for the synthesis of poly(4-acetoxystyrene) and poly(4-acetoxystyrene)-block-polystyrene by bulk, solution and emulsion techniques. *Macromol Rapid Commun* 2001;22:1076–80.
- [112] Stenzel MH, Cummins L, Roberts GE, Davis TP, Vana P, Barner-Kowollik C. Xanthate mediated living polymerization of vinyl acetate: a systematic variation in MADIX/RAFT agent structure. *Macromol Chem Phys* 2003;204:1160–8.
- [113] Qi G, Jones CW, Schork FJ. RAFT inverse miniemulsion polymerization of acrylamide. *Macromol Rapid Commun* 2007;28:1010–6.
- [114] Prescott SW, Ballard MJ, Rizzardo E, Gilbert RG. Successful use of RAFT techniques in seeded emulsion polymerization of styrene: living character, RAFT agent transport, and rate of polymerization. *Macromolecules* 2002;35:5417–25.
- [115] Prescott SW, Ballard MJ, Rizzardo E, Gilbert RG. Radical loss in RAFT-mediated emulsion polymerizations. *Macromolecules* 2005;38:4901–12.
- [116] Smulders W, Gilbert RG, Monteiro MJ. A kinetic investigation of seeded emulsion polymerization of styrene

- using reversible addition–fragmentation chain transfer (RAFT) agents with a low transfer constant. *Macromolecules* 2003;36:4309–18.
- [117] Prescott SW, Ballard MJ, Rizzardo E, Gilbert RG. Rate optimization in controlled radical emulsion polymerization using RAFT. *Macromol Theory Simul* 2006;15:70–86.
- [118] Peklak AD, Butte A. Kinetic model of reversible addition fragmentation chain transfer polymerization of styrene in seeded emulsion. *J Polym Sci Part A: Polym Chem* 2006;44:6114–35.
- [119] Nozari S, Tauer K. Calorimetric study on the influence of the nature of the RAFT agent and the initiator in ab initio aqueous heterophase polymerization. *Polymer* 2005;46:1033–43.
- [120] Tauer K, Nozari S, Ali AMI. Experimental reconsideration of radical entry into latex particles. *Macromolecules* 2005;38:8611–3.
- [121] Nozari S, Tauer K, Ali AMI. RAFT agent concentration in polymer particles during emulsion polymerization. *Macromolecules* 2005;38:10449–54.
- [122] Luo Y, Cui X. Reversible addition–fragmentation chain transfer polymerization of methyl methacrylate in emulsion. *J Polym Sci Part A: Polym Chem* 2006;44:2837–47.
- [123] Urbani CN, Nguyen HN, Monteiro MJ. RAFT-mediated emulsion polymerization of styrene using a non-ionic surfactant. *Aust J Chem* 2006;59:728–32.
- [124] Ferguson CJ, Hughes RJ, Pham BTT, Hawkett BS, Gilbert RG, Serelis AK, et al. Effective ab initio emulsion polymerization under RAFT control. *Macromolecules* 2002;35:9243–5.
- [125] Ferguson CJ, Hughes RJ, Nguyen D, Pham BTT, Gilbert RG, Serelis AK, et al. Ab initio emulsion polymerization by RAFT-controlled self-assembly. *Macromolecules* 2005;38:2191–204.
- [126] Gilbert RG. Particle formation by self-assembly in controlled radical emulsion polymerizations. *Macromolecules* 2006;39:4256–8.
- [127] Freal-Saison S, Save M, Bui C, Charleux B, Magnet S. Emulsifier-free controlled free-radical emulsion polymerization of styrene via RAFT using dibenzyltrithiocarbonate as a chain transfer agent and acrylic acid as an ionogenic comonomer: batch and spontaneous phase inversion processes. *Macromolecules* 2006;39:8632–8.
- [128] Monteiro MJ, Adamy MM, Leeuwen BJ, van Herk AM, Destarac M. A “living” radical ab initio emulsion polymerization of styrene using a fluorinated xanthate agent. *Macromolecules* 2005;38:1538–41.
- [129] Manguian M, Save M, Charleux B. Batch emulsion polymerization of styrene stabilized by a hydrophilic macro-RAFT agent. *Macromol Rapid Commun* 2006;27:399–404.
- [130] Hartmann J, Urbani C, Whittaker MR, Monteiro MJ. Effect of degassing on surfactant-free emulsion polymerizations of styrene mediated with RAFT. *Macromolecules* 2006;39:904–7.
- [131] Liu S, Hermanson KD, Kaler EW. Reversible addition–fragmentation chain transfer polymerization in microemulsion. *Macromolecules* 2006;39:4345–50.
- [132] Hermanson KD, Liu S, Kaler EW. Kinetic modeling of controlled living microemulsion polymerizations that use reversible addition–fragmentation chain transfer. *J Polym Sci Part A: Polym Chem* 2006;44:6055–70.
- [133] Biasutti JD, Davis TP, Lucien FP, Heuts JPA. Reversible addition–fragmentation chain transfer polymerization of methyl methacrylate in suspension. *J Polym Sci Part A: Polym Chem* 2005;43:2001–12.
- [134] Lansalot M, Farcet C, Charleux B, Vairon J, Pirri R. Controlled free-radical miniemulsion polymerization of styrene using degenerative transfer. *Macromolecules* 1999;32:7354–60.
- [135] Farcet C, Lansalot M, Pirri R, Vairon JP, Charleux B. Polystyrene-block-poly(butyl acrylate) and polystyrene-block-poly[(butyl acrylate)-*co*-styrene] block copolymers prepared via controlled free-radical miniemulsion polymerization using degenerative iodine transfer. *Macromol Rapid Commun* 2000;21:921–6.
- [136] Apostolo M, Arcella V, Storti G, Morbidelli M. Free radical controlled polymerization of fluorinated copolymers produced in microemulsion. *Macromolecules* 2002;35:6154–66.
- [137] Lyons DF. The effect of molecular weight on properties of fluoroelastomers cured with bisphenol AF. Technical Papers—American Chemical Society, Rubber Division, Spring Technical Meeting, San Francisco, CA, USA, April 28–30, 2003. p. 104–32.
- [138] Song J, Winnik MA. Monodisperse, micron-sized reactive low molar mass polymer microspheres by two-stage living radical dispersion polymerization of styrene. *Macromolecules* 2006;39:8318–25.
- [139] Tonnar J, Lacroix-Desmazes P, Boutevin B. Controlled radical ab initio emulsion polymerization of *n*-butyl acrylate by reverse iodine transfer polymerization (RITP): effect of the hydrolytic disproportionation of iodine. *Macromol Rapid Commun* 2006;27:1733–8.
- [140] Tonnar J, Lacroix-Desmazes P, Boutevin B. Controlled radical polymerization of styrene by reverse iodine transfer polymerization (RITP) in miniemulsion: use of hydrogen peroxide as oxidant. *Macromolecules* 2007;40:186–90.
- [141] Pouget E, Tonnar J, Eloy C, Lacroix-Desmazes P, Boutevin B. Synthesis of poly(styrene)-*b*-poly(dimethylsiloxane)-*b*-poly(styrene) triblock copolymers by iodine transfer polymerization in miniemulsion. *Macromolecules* 2006;39:6009–16.
- [142] Enright TE, Cunningham MF, Keoshkerian B. Nitroxide-mediated polymerization of styrene in a continuous tubular reactor. *Macromol Rapid Commun* 2005;26:221–5.
- [143] Russum JP, Jones CW, Schork FJ. Impact of flow regime on polydispersity in tubular RAFT miniemulsion polymerization. *AIChE J* 2006;52:1566–76.
- [144] Russum JP, Jones CW, Schork FJ. Continuous living polymerization in miniemulsion using reversible addition fragmentation chain transfer (RAFT) in a tubular reactor. *Ind Eng Chem Res* 2005;44:2484–93.
- [145] Russum JP, Jones CW, Schork FJ. Continuous reversible addition–fragmentation chain transfer polymerization in miniemulsion utilizing a multi-tube reaction system. *Macromol Rapid Commun* 2004;25:1064–8.
- [146] Smulders WW, Jones CW, Schork FJ. Continuous RAFT miniemulsion polymerization of styrene in a train of CSTRs. *AIChE J* 2005;51:1009–21.
- [147] Smulders WW, Jones CW, Schork FJ. Synthesis of block copolymers using RAFT miniemulsion polymerization in a train of CSTRs. *Macromolecules* 2004;37:9345–54.