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ARTICLE

Miniemulsion Polymerization with Arrested Ostwald Ripening Stabilized by Amphiphilic RAFT Copolymers

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ABSTRACT: We describe a method and conditions for the preparation of monodisperse latex particle dispersions using low molecular-weight, amphiphilic styrene-*b*-acrylic acid macro-RAFT diblock copolymers as sole stabilizers. The macro-RAFT copolymers are soluble in styrene monomer droplets when the acrylic acid is in its neutral, protonated form, but adsorb irreversibly at the interface between the monomer droplets and the aqueous phase to form an insoluble monolayer when conditions favor deprotonation. Droplets thus stabilized exhibited no coarsening by Ostwald ripening over at least several days. Polymerization yielded a one-to-one correspondence between the size of the initial droplets and the resultant latex particles, consistent with ideal miniemulsion polymerization, when the least labile macro-RAFT stabilizer was used. GPC analysis of molecular weights showed that in all cases the polymerization remained under RAFT control. The approach described enables true miniemulsion polymerization to proceed in the absence of both free surfactant and hydrophobic stabilizer.

Introduction

The miniemulsion polymerization process, in which monomer droplets provide the main locus of particle nucleation and growth, was first described by Ugelstad et al. in the 1970s.[1] Polymerization in an ideal miniemulsion system yields a one-to-one correspondence between the initial distribution of droplets and the final polymer latex particles produced. In order to achieve this ideal the droplets need to be stabilized against coalescence and coarsening by Ostwald ripening. Moreover, polymerization needs to proceed in a way that avoids the formation of secondary particles. A surfactant, frequently sodium dodecyl sulfate (SDS), is generally included in the formulation to prevent droplet coalescence and a water insoluble hydrophobic species, frequently hexadecane, is included as a costabilizer to provide an osmotic pressure barrier to Ostwald ripening. If coalescence is avoided, then droplet number can also be preserved as particle number by the incorporation of a preformed hydrophobic polymer.[2−5] An excellent comprehensive review of miniemulsion polymerizations, including droplet stabilization and mechanisms of particle formation has been presented by Landfester.[6]

Relative to conventional emulsion polymerization, miniemulsion polymerization has a number of disadvantages, such as the need for relatively high shear to generate small droplets, more polydisperse particles and difficulties controlling the exotherm of an "all in" process on a large scale. However, miniemulsion polymerization has the advantage that moieties that are too insoluble in water to readily transport through the continuous phase can be incorporated into the final latex particles. Thus, there is potential for miniemulsion polymerization to be used for the encapsulation of solid species such as pigments, in the encapsulation and delivery of very hydrophobic drugs, and for production of polymer particles with designed compositions,[7−21] which are not readily achieved using conventional emulsion polymerization. Recently, amphiphilic copolymers have been used to replace surfactants as droplet stabilizers,[7,8,22−25] becoming incorporated into polymerized particles as electrosteric stabilizers, but these systems retain the need for a hydrophobic costabilizer like hexadecane. Such copolymers have been synthesized by a number of different methods, but those obtained from controlled or living radical polymerizations were well-defined and monodisperse in their molecular weight.[26,27]

Apart from our own earlier work,[28] there have been few attempts to synthesize polymer particles without costabilizer.[22,25,28] Baskar et al.[22] and Manguian et al.[25] have both reported producing stable latexes using comb-like amphiphilic copolymers. Those used by Baskar et al.[22] were high molecular weight (approximately 4 × 10^4 Da), randomly distributed and fairly polydisperse. Surface coverage and surface tension of the final latex particles was studied. Those used by Manguian et al.[25] were said to be readily water-soluble and thus could be transportable through the aqueous phase between droplets. In both systems, droplet stability was only studied by visual observation, and neither paper demonstrated a one-to-one correspondence between droplets and final particles.

The miniemulsion polymerization process has been used to facilitate molecular weight control in dispersed phase polymerization using water-insoluble RAFT agents.[29−31] As demonstrated in our previous communication,[28] water-insoluble living RAFT block copolymers of styrene/acrylic acid and butyl acrylate/acrylic acid can be used as sole stabilizers of miniemulsion droplets and particles while simultaneously controlling molecular weight, producing polymer latexes with narrow particle size distributions.

The purpose of this paper is to elucidate the conditions and mechanism by which these amphiphilic macro-RAFT copolymers (Figure 1b) stabilize monomer emulsion droplets, allowing ideal miniemulsion polymerization to occur without a costabilizer. The influence of hydrophobic and hydrophilic block lengths of amphiphilic RAFT-poly(styrene-*b*-acrylic acid) and monomer/RAFT

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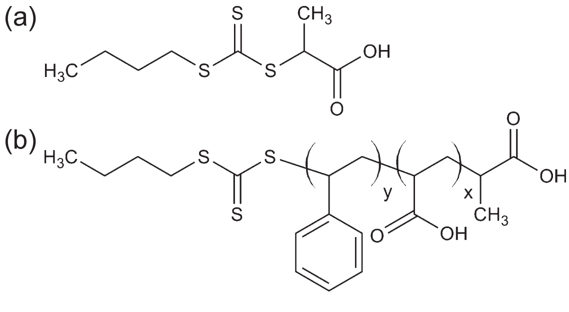

Figure 1. Structures of (a) RAFT agent and of (b) amphiphilic macro-RAFT diblocks of poly(styrene-*b*-acrylic acid) used for miniemulsion polymerizations; average degrees of polymerization, *x* and *y*, are given in Table 1.

ratio on the stability of miniemulsion droplets and the characteristics of the final latexes is also described.

Experimental Section

Materials. Milli-Q water was used in the synthesis of all latexes. Acrylic acid (AA, Sumika) and 1,4-dioxane (Fluka) were distilled under reduced pressure. Styrene (Sty, Synthetic Resins) had the inhibitor removed by passing it through an inhibitor removal column (Aldrich). 2,2′-Azobis(isobutyronitrile) (AIBN, Fluka) was recrystallized from ethanol. 4,4′-Azobis(4-cyanovaleric acid) (V-501, Wako), sodium hydroxide (NaOH, Aldrich), methanol (MeOH, Ajax, HPLC grade) and tetrahydrofuran (THF, Ajax, HPLC grade) were used as received. The RAFT agent 2-{[(butylsulfanyl)carbonothioyl]sulfanyl}propanoic acid (Figure 1a), was synthesized as previously described.[26]

Synthesis of Amphiphilic RAFT-Capped Diblocks. Acrylic acid and styrene were polymerized in the presence of the RAFT agent to give amphiphilic diblocks (Figure 1b) with different hydrophilic and hydrophobic block lengths (Table 1) in a two-stage reaction. In stage one the desired number of acrylic acid units was added to the RAFT agent in dioxane at 70 °C under nitrogen, using V-501 as initiator, at the RAFT/V-501 ratios between 2.5 and 10, as shown in Table 1. Target final solids content was around 40% by weight and the first stage reactions were generally complete in 2 h. A sample was withdrawn at the end of this stage for gravimetric determination of solids content and electrospray mass spectrometry. This showed that the reactions had gone to completion and the expected average degree of polymerization had been attained. The desired amount of styrene, V-501 and dioxane was then added to the reaction mixture, to give a diblock copolymer solution with a target final solids content of 40%. The polymerization with styrene was carried out overnight at 70 °C under nitrogen pressure to produce the required amphiphilic diblock copolymers. The length of styrene hydrophobic blocks was checked by gravimetry and GPC. Most of the dioxane was removed from the final copolymer solutions by purging nitrogen through the solution while it was being stirred overnight on a magnetic stirrer in a fume hood. The copolymers were then dried in a vacuum oven at 60 °C until solvent-free copolymer was obtained.

The synthesis of RAFT-$Sty_{15}AA_5$ is used as a typical example. RAFT agent (0.80 g, 3.36×10^{-3} mol), V501 (0.09 g, 0.33×10^{-3} mol), acrylic acid (1.21 g, 16.86×10^{-3} mol) and dioxane (2.15 g) were mixed in round-bottom flask. The mixture was stirred at room temperature (until both RAFT agent and initiator were completely dissolved), deoxygenated with nitrogen gas (5 min), and then immersed in a heated oil bath at 60 °C for 2 h. The flask was then cooled down to room temperature and styrene (6.93 g, 66.54×10^{-3} mol), V501 (0.28 g, 1.01×10^{-3} mol) and 12.05 g of dioxane were added. The mixture was deoxygenated and reacted for at least 2 h at 80 °C. A yellow powder of RAFT-$Sty_{15}AA_5$ was obtained after dioxane was removed.

Table 1. Compositions of Sty/AA Diblock Copolymer Stabilizers

stabilizer	RAFT/ V-501	AA/RAFT	Sty/RAFT added	Sty/RAFT by GPC
RAFT-$Sty_{15}AA_5$	2.5	5	20	15
RAFT-$Sty_{24}AA_5$	3.3	5	30	24
RAFT-$Sty_{28}AA_{20}$	2.8	20	30	28
RAFT-Sty_5AA_{12}	9.7	12	5	N/A

Electrospray mass spectrometry was carried out on a Finnigan LCQ MS detector with Finnigan LCQ Data Processing using instrument control software. A 10 μg sample of the final reaction product was dissolved in 10 mL of methanol for electrospray mass spectrometry and 20 μL of this solution was fed into the electrospray ionization unit at 0.05 mL/min.

Gel permeation chromatography (GPC) was carried out using a Shimadzu system fitted with Waters HR4, HR3, and HR2 columns, 5% acetic acid in tetrahydrofuran as eluent,[26,32] polystyrene standards, refractive index detection and Polymer Laboratories Cirrus software. Detailed procedures have been described previously.[26]

Miniemulsion Preparation. Although the approach used can generate latexes at appreciably higher solids contents (> 25%), those used in this work were prepared at approximately 1% solids. This was so that both the droplet and the final latex particle sizes could be measured by light scattering without dilution of the sample, thus avoiding any errors associated with dilution. The required amount of macro-RAFT diblock was dissolved in styrene monomer. Water and NaOH were then added and the mixture was emulsified for 1 h using a magnetic stirrer. The emulsion thus obtained was chilled in ice water and further emulsified by ultrasonication for 20 min using a Vibra-Cell ultrasonic processor (Sonics and Materials, Inc.), with a standard probe at 30% amplitude.

Once emulsification was complete the droplet size was measured as a function of time using a high performance particle sizer (HPPS, Malvern Instruments Limited). The particle size of the final latexes was also determined by HPPS, and by capillary hydrodynamic fractionation (CHDF1100, Matec Applied Sciences, cartridge C560, at a detector wavelength of 200 or 220 nm, eluent GR500). Particle size distributions and particle morphology were determined by transmission electron microscopy (TEM, Biofilter, Philips).

Miniemulsion Polymerization. Miniemulsion polymerizations were carried out using four amphiphilic macro-RAFT agents under a variety of initial conditions listed in Table 2 as follows: The required amount of diblock was dissolved in styrene monomer. Water and NaOH were then added and the mixture was emulsified for 1 h using a magnetic stirrer. The emulsion thus obtained was chilled in ice water and further emulsified by ultrasonication for 20 min using a Vibra-Cell ultrasonic processor (Sonics and Materials, Inc.), with a standard probe at 30% amplitude. A sample was taken to monitor droplet size with time, using the HPPS. The miniemulsion was transferred to a 50 mL round-bottom flask containing the required amount of AIBN initiator. The flask was sealed with a rubber septum, stirred magnetically, deoxygenated by nitrogen purging for 10 min, and then immersed in an oil bath at 70 °C for 4 h to effect polymerization.

Miniemulsion polymerization, using RAFT-$Sty_{15}AA_5$ macro-RAFT agent as a sole stabilizer, is used as a typical example. Dry macro-RAFT agent (0.03 g, 0.01×10^{-3} mmol) was dissolved in styrene (0.44 g, 4.23 mmol), which was followed by an addition of water (40.13 g) and NaOH (2.4 mg, 0.06×10^{-3} mmol), in a beaker and stirred for 30 min. The mixture was then chilled in ice water and ultrasonicated for 20 min using a Vibra-Cell ultrasonic processor (Sonics and Materials, Inc.), with a standard probe at 30% amplitude. The miniemulsion was transferred to a 50 mL round-bottom flask containing AIBN (0.01 g, 0.07 mmol) initiator. The flask was sealed with a rubber septum, stirred magnetically and deoxygenated by N_2 purging

Table 2. Miniemulsion Polymerizations of Styrene using Non-Labile Macro-RAFT Diblock Copolymers as Sole Stabilizers

			z-average diameters (nm)		number-average diameters D_n (nm) (CHDF)
stabilizer	Sty/ RAFT	NaOH/ RAFT	droplet	particle	particle
RAFT-$Sty_{15}AA_5$	69	5.4	104	82	46
	102	6.4	96	76	45
	198	4.0	60	63	37
	292	4.7	65	70	40
	388	5.5	59	60	35
	491	8.7	76	70	36
	617	6.6	60	67	45
RAFT-$Sty_{24}AA_5$	70	6.3	170	166	61
	98	5.8	101	102	53
	214	6.8	73	74	37
	303	6.3	64	64	
	399	6.6	60	60	40
	512	6.3	62	62	40
	597	6.6	59	59	38
RAFT-$Sty_{28}AA_{20}$	67	19.1	119	122	40
	101	19.6	119	63	38
	201	19.5	117	80	40
	299	19.3	68	54	44
	411	21.4	52	55	44
	484	20.7	59	55	44
	621	21.4	73	56	43

for 10 min, and then immersed in an oil bath at 70 °C for at least 4 h. The mass of macro-RAFT agent on monomer used in this synthesis was approximately 7%. Although this is a little high in conventional terms, we need to bear in mind that there is no free surfactant in the system and all the macro-RAFT agent present becomes part of the polymer of the latex.

Results and Discussion

Droplet Stability and Arrested Ripening. The stability of miniemulsion monomer droplets incorporating each of the amphiphilic macro-RAFT agents RAFT-$Sty_{15}AA_5$, RAFT-$Sty_{24}AA_5$, RAFT-$Sty_{28}AA_{20}$ and RAFT-Sty_5AA_{12} was studied as a function of concentration and solution conditions. If the miniemulsion droplets were stable for a long period of time, it was deemed to be more likely that the droplets would maintain their integrity throughout the course of the polymerization. HPPS measurements for droplets containing amphiphilic macro-RAFT agents at a molar ratio of 1 to 300 styrene are shown in Figure 2. This clearly shows that the average diameters of droplets containing RAFT-$Sty_{15}AA_5$, RAFT-$Sty_{24}AA_5$ and RAFT-$Sty_{28}AA_{20}$ (as shown in Figure 2A) are virtually independent of the choice of amphiphilic diblock, and do not change measurably over 1 h. In many cases the droplet diameters do not change over 10 days or longer (see below). In contrast, droplets containing RAFT-Sty_5AA_{12} are initially larger, and undergo a quite rapid increase in diameter with time. The rate of increase in droplet volume, $(r/r_0)^3$, in this system (as shown in Figure 2B) is linear. This is considered reasonable proof that the mechanism for the size increase in this system is Ostwald ripening.[33]

This suggests that the more hydrophobic amphiphilic macro-RAFT agents are not only effective as electrosteric stabilizers, but also prevent droplet growth by Ostwald ripening. The concentration of amphiphilic macro-RAFT agent that remains dissolved in the monomer droplets is too low to act as a conventional osmotic agent or costabilizer. It thus appears that the insoluble monolayer itself resists Ostwald ripening pressures, even with small droplets and fairly broad particle size distributions, resulting in exceedingly stable droplets.

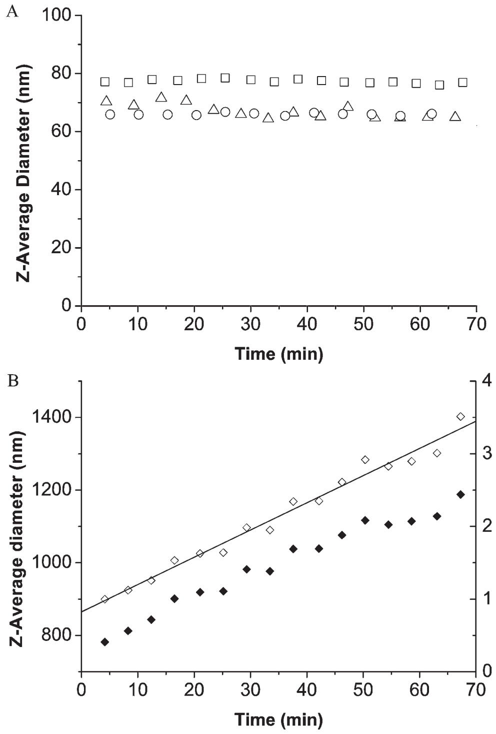

Figure 2. *z*-Average diameters of styrene droplets stabilized by various amphiphilic macro-RAFT agents used in this work, measured by HPPS as a function of time, for molar ratios of styrene/amphiphilic RAFT agent closest to 300: (A) RAFT-$Sty_{15}AA_5$ stabilized droplets (△), RAFT-$Sty_{24}AA_5$ stabilized droplets (□), RAFT-$Sty_{28}AA_{20}$ stabilized droplets (○) and (B) RAFT-Sty_5AA_{12} stabilized droplets (◆). The volume, i.e., the ratio r^3/r_o^3 (◇) of the droplets stabilized by the labile diblock RAFT-Sty_5AA_{12} increases linearly with time, indicating Ostwald ripening.

Emulsion stabilization by an insoluble monolayer arresting Ostwald ripening has been proposed previously. Conventional emulsifiers coexist and are assumed to rapidly equilibrate with a continuous phase concentration, so that the interfacial tension remains constant for all droplet sizes. In essence the chemical potential of a soluble emulsifier is fixed, so that the emulsion reduces to a two-component system. An insoluble monolayer fixes the total amount of available emulsifier, and the amount on each droplet, so that the chemical potential of the emulsifier and hence the interfacial tension on the droplet changes when a droplet grows or shrinks.

Swelling of droplets coated with an insoluble monolayer increases the surface area, A, and also the interfacial tension, γ. Droplet shrinkage is similarly accompanied by a decrease in interfacial tension and reduced driving force for further dissolution of contents. A sufficiently high surface elasticity

$$E = A\frac{\partial \gamma}{\partial A} > \frac{\gamma}{2}$$

can in principle completely arrest ripening.[34−36]

These amphiphilic RAFT copolymers satisfy the essential criteria for generating such insoluble monolayers. During miniemulsion preparation, they are dissolved into styrene monomer with the acrylic acid units in their uncharged (protonated) form. When mixed with the basic aqueous continuous phase, the acrylic acid units adsorb at the styrene/water interface where they are neutralized, forming an anionic electrosteric stabilizing layer that protects droplets

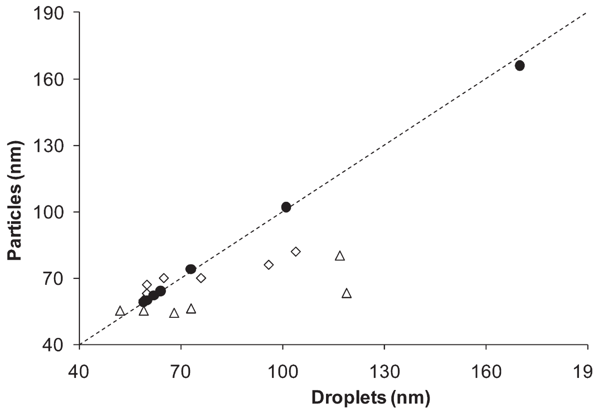

Figure 3. *z*-Average diameters of final latex particles versus original monomer droplets, stabilized by RAFT-$Sty_{24}AA_5$ (●), RAFT-$Sty_{15}AA_5$ (◇), and RAFT-$Sty_{28}AA_{20}$ (△). Line shows ideal miniemulsion polymerization condition where particle and droplet diameters are equal.

from coalescence, but also prevents the copolymer from redissolving into the droplet. If the polystyrene block is sufficiently long, then the amphiphilic diblock is also water-insoluble and hence nonlabile, forming an insoluble monolayer on the droplet surface. Thus, the focus is on the ratio of chain lengths rather than the absolute length of either block.

A similar stabilizing effect has been reported for protein-stabilized emulsions, although no complete arrest of Ostwald ripening has been reported for proteins.[37] This has been suggested to be due to the finite desorption rate of proteins into the continuous phase, which means that the surface tension is regulated.

Ostwald ripening has been successfully arrested in Pickering emulsions[38] and this is attributed to a combination of factors including their effectively irreversible deposition at the interface (which depends on particle size and contact angle) as well as on the possible formation of a rigid coating of "jammed" particles. The idea of mechanically stabilizing emulsion droplets has also been explored, e.g., using SDS/chitosan mixed surface coatings.[39] Theoretical predictions of mechanical stability suggest that such a rigid layer thickness needs to be of order 50% of the droplet radius. Such a mechanical stabilization cannot be operating here, where the fully extended styrene and acrylic acid chains sum to only about 8 nm or 10−20% of the droplet radius.

The present system is to our knowledge the first time an insoluble molecular adsorbed layer has been used to arrest Ostwald ripening. The acid−base chemistry of these copolymers suggests it as a general method for irreversibly adsorbing amphiphilic molecules into a nonlabile film for emulsion stabilization without the need for an oil-soluble costabilizer.

Figure 4 shows the droplet diameters determined by HPPS for the RAFT-$Sty_{24}AA_5$ stabilized miniemulsions at styrene to macro-RAFT agent mole ratios ranging from approximately 70 to 600 (see Table 2) over the first hour after formation. At all compositions the average droplet diameter was constant for this period, and remained so or slightly decreased if left for up to 10 days (Figure 5).

As reported previously,[28] droplet sizes determined by light scattering decreased with increasing styrene to amphiphilic macro-RAFT ratio, contrary to what might generally be expected. Figure 6 shows that the same behavior was observed for all three insoluble monolayer-forming (nonlabile) amphiphilic copolymers. The same trend is also observed for the particles formed by polymerization, and will be discussed further below.

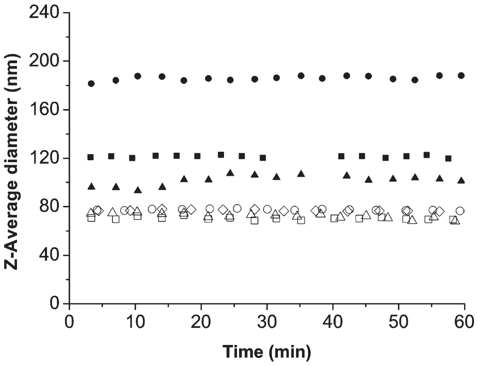

Figure 4. Diameter of styrene droplets stabilized by the RAFT-$Sty_{24}AA_5$ diblock, measured by HPPS as a function of time, for molar ratios of styrene to diblock of 70 (●), 98 (■), 214 (▲), 303 (●), 399 (◇), 512 (□), and 597 (△).

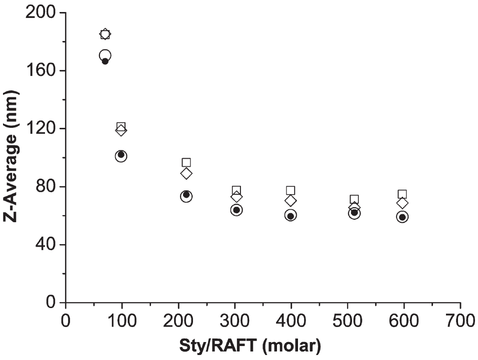

Figure 5. *z*-Average diameters (HPPS) for resultant particles and droplets as a function of time for RAFT-$Sty_{24}AA_5$ stabilized miniemulsions with various styrene/RAFT ratios: droplets at 0 min (○), droplets after 120 min (◇), droplets after 10 days (□), and final particles (●).

Ideal Miniemulsion Polymerization. Figures 5 and 6 show the *z*-average diameters of droplets and latex particles formed from miniemulsions stabilized by a nonlabile amphiphilic diblock copolymer layer. As the monomer droplets were stable over time (Figures 2A, 4 and 5), and the final polymer particles had very similar sizes to the corresponding initial monomer droplets (see Figures 3, 5 and 6), we conclude that the identities of the monomer droplets are preserved throughout the polymerization, yielding a one to one correspondence between droplets and polymer particles when the least labile macro-RAFT stabilizer was used. Since each droplet is stabilized by nonlabile amphiphilic macro-RAFT agents that are also effective electrosteric stabilizers, the droplet number is necessarily preserved as particle number. For the emulsion stabilized by the labile diblock RAFT-Sty_5AA_{12}, the droplets were very unstable as shown in Figure 2. Polymerization reaction therefore was not carried out.

Particle number and weight distributions were determined for particles prepared at various ratios of styrene to amphiphilic RAFT agents by CHDF. Representative number and weight distributions for particles stabilized by RAFT-$Sty_{24}AA_5$ at different concentrations are shown in Figure 7. At the lowest RAFT concentrations the particle size distributions are narrow and symmetric, but at higher RAFT concentrations we find that the distribution broadens and becomes skewed due to the presence of a few larger particles. Although the effect is small in the number distribution, it is significant in the weight distribution and these few large particles would completely dominate the *z*-distribution measured by dynamic light scattering, which depends on

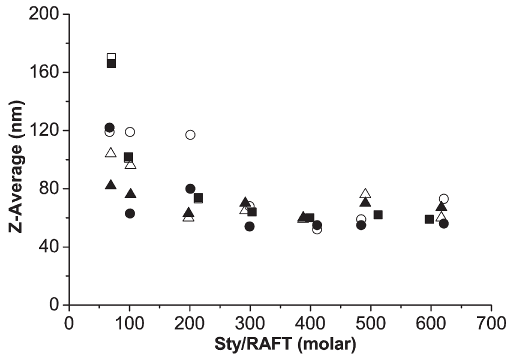

Figure 6. *z*-Average droplet and resultant particle diameters (HPPS) as a function of styrene/RAFT molar ratio for miniemulsions using various the non labile amphiphilic RAFT stabilizers: RAFT-Sty$_{15}$AA$_5$ stabilized droplets (△), RAFT-Sty$_{15}$AA$_5$ stabilized particles (▲), RAFT-Sty$_{24}$AA$_5$ stabilized droplets (☐), RAFT-Sty$_{24}$AA$_5$ stabilized particles (■), RAFT-Sty$_{28}$AA$_{20}$ stabilized droplets (○), and RAFT-Sty$_{28}$AA$_{20}$ stabilized particles (●).

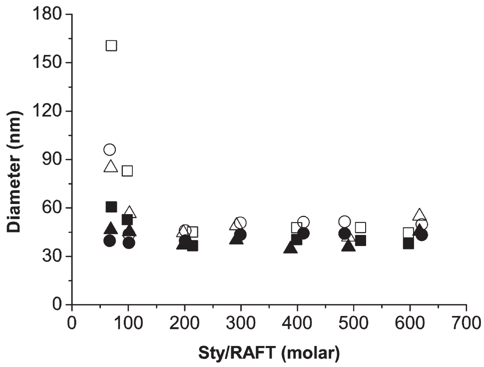

Figure 8. Particle sizes measured by CHDF for latexes stabilized by the nonlabile amphiphilic macro-RAFT copolymers at different molar ratios of Sty/RAFT: RAFT-Sty$_{15}$AA$_5$, number-average diameter (▲); RAFT-Sty$_{15}$AA$_5$, weight-average diameter (△); RAFT-Sty$_{24}$AA$_5$, number-average diameter (■), RAFT-Sty$_{24}$AA$_5$, weight-average diameter (☐); RAFT-Sty$_{28}$AA$_{20}$, number-average diameter (●), RAFT-Sty$_{28}$AA$_{20}$, and weight-average diameter (○).

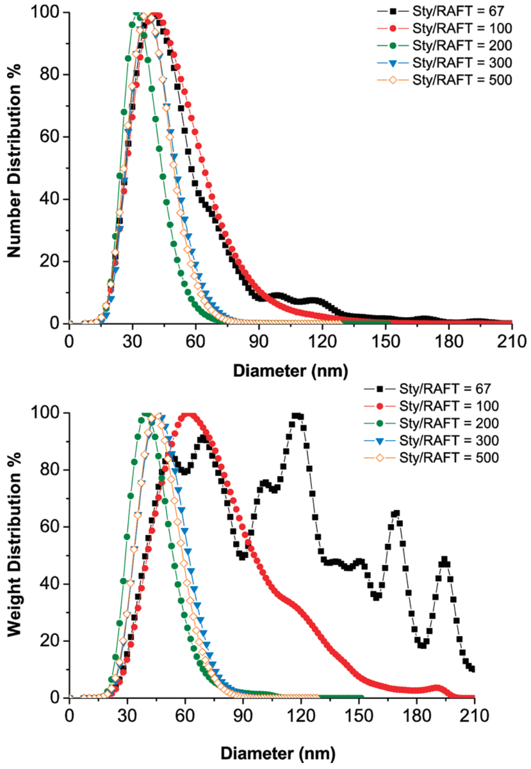

Figure 7. CHDF measurements showing number distribution (A) and weight distribution (B) for latex particles stabilized by the RAFT-Sty$_{24}$AA$_5$ diblock at different ratios to styrene: 1 to 70, 98, 303, 512, and 597 as shown on the graphs.

the square of the particle (hydrodynamic) volume. Similar results and trends were obtained for all nonlabile stabilizers examined.

Figure 8 summarizes the number- and weight-average particle diameters of latex particles formed from miniemulsions stabilized by all the nonlabile amphiphilic copolymers used as sole stabilizers in this study as a function of styrene to amphiphilic macro-RAFT ratios. At low RAFT concentrations the number- and weight-average diameters agree well with each other, and with the dynamic light scattering results (Figures 4, 5 and 6), as would be expected for a narrow size distribution. The number-average diameter is little affected by either the choice of nonlabile stabilizer or by styrene/RAFT ratio, even at high RAFT concentrations where the distribution is noticeably skewed. However the skewed distribution increases the weight-average diameter markedly at high RAFT concentrations for all macro-RAFT agents, although the effect depends to some extent on the amphiphilic diblock copolymer.

The observed latex particle size distribution is thus determined directly from the original distribution of emulsion droplets, which itself depends on the type and concentration of amphiphilic diblock used as stabilizer. This situation contrasts markedly with emulsion polymerization using water-soluble and micelle-forming analogs of these amphiphilic diblocks.[40] At sufficiently low copolymer concentrations (Sty/RAFT >200), the latex particles were small and had narrow size distributions. CHDF results are confirmed by TEM micrographs shown in Figures 9 and 10. Figure 9 shows a narrow distribution of latex particle sizes formed by polymerization of miniemulsions stabilized by the two nonlabile amphiphilic copolymers, RAFT-Sty$_{24}$AA$_5$ and RAFT-Sty$_{28}$AA$_{20}$, with styrene/RAFT > 400.

Figure 10D shows a similarly narrow size distribution of latex particle sizes formed using RAFT-Sty$_{24}$AA$_5$ at styrene/RAFT > 200. The particles formed from miniemulsions containing high concentrations of amphiphilic diblock stabilizer, however, contain some large particles as expected from CHDF measurements. Parts A and C of Figure 10 show representative TEM micrographs of polymer particles stabilized by RAFT-Sty$_{24}$AA$_5$ at styrene/RAFT < 100, and reveal the existence of a number of large, hollow or multihollow particles. These unwanted morphological characteristics were most likely formed during the dispersion process at high amphiphile concentrations as multiple (water-in-oil-in-water) emulsions. As with polymerization at lower amphiphile concentrations, these structures are also preserved during polymerization. A similar effect, the burying of copolymer stabilizer inside latex particles, was postulated by Houillot et al.,[24] although no solid evidence was presented. Such particles explain the anomalous dependence of droplet and particle size on amphiphilic block copolymer concentration. The very nonlabile nature of the amphiphilic copolymers can stabilize water droplets within a larger oil droplet, although such large structures could very likely be broken apart by shearing for longer and/or at a higher rate.

This interpretation is also supported by the absence of such complex morphologies when only one-sixth of the amount of NaOH required to fully ionize the poly(acrylic acid) block was used in the emulsification step (Figure 10B).

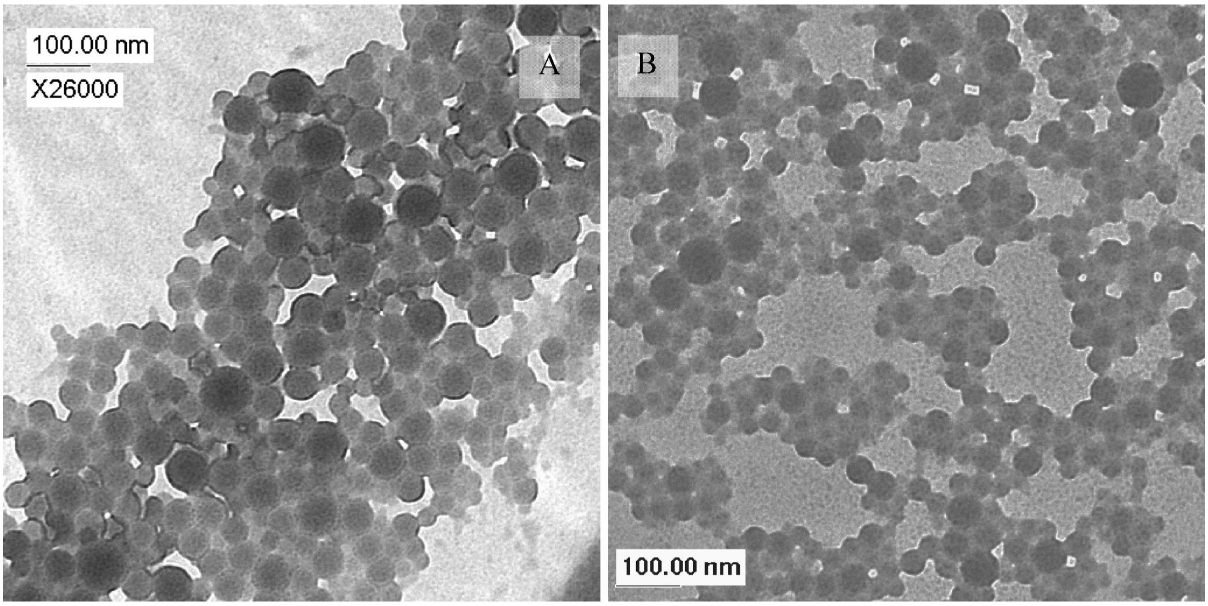

Figure 9. TEM micrographs of polymer particles stabilized by RAFT-Sty$_{24}$AA$_5$ (A) and RAFT-Sty$_{28}$AA$_{20}$ (B) at mole ratios of Sty/RAFT of 403 and 409.

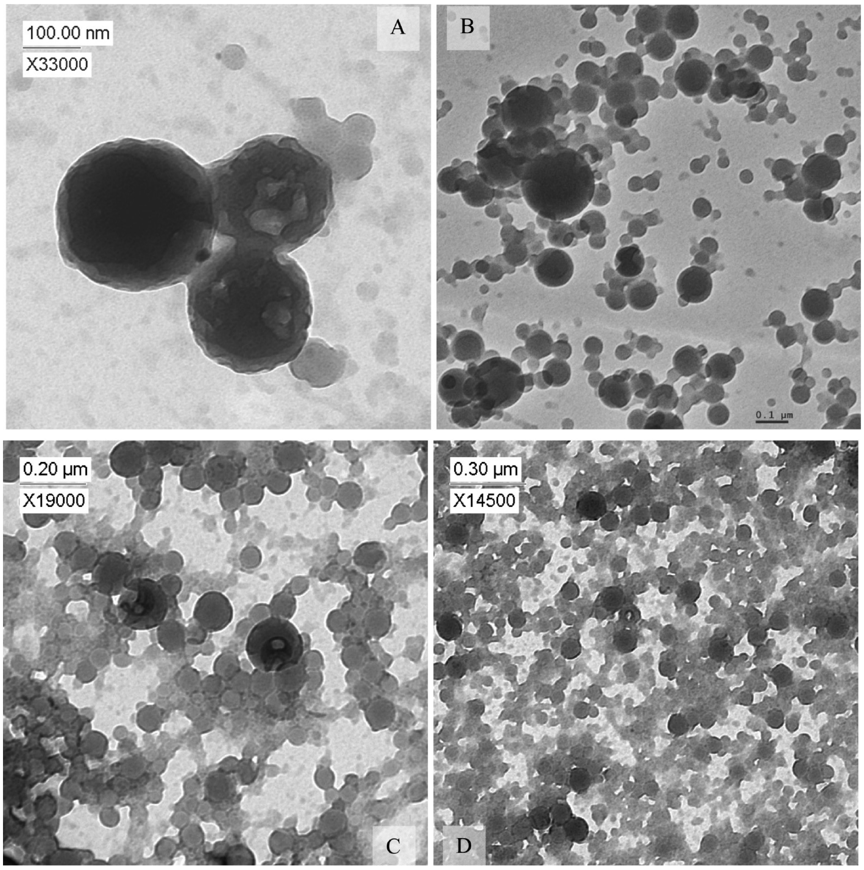

Figure 10. TEM micrographs of polymer particles stabilized by different amount of the RAFT-Sty$_{24}$AA$_5$ diblock for mole ratios of Sty/RAFT of 70 (A, at NaOH/RAFT = 6), of 70 (B, at NaOH/RAFT = 1), of 98 (C) and of 213 (D).

Under these circumstances the surface-active diblocks may remain soluble in the monomer droplets, and the amount adsorbed at the interface acting as stabilizers is expected to be much lower.

RAFT Control of Polymerization. In these systems each amphiphilic copolymer is not only a nonlabile electrosteric stabilizer, but also a macro-RAFT agent that mediates the growth of the polymer chains within the droplets. Since there is no free surfactant in these systems to stabilize new particles and the nonlabile copolymers are not present in the continuous phase micellar nucleation should be absent. Moreover, any new particles nucleated in these systems would not contain RAFT agents and would necessarily grow by conventional emulsion polymerization. GPC analysis of the

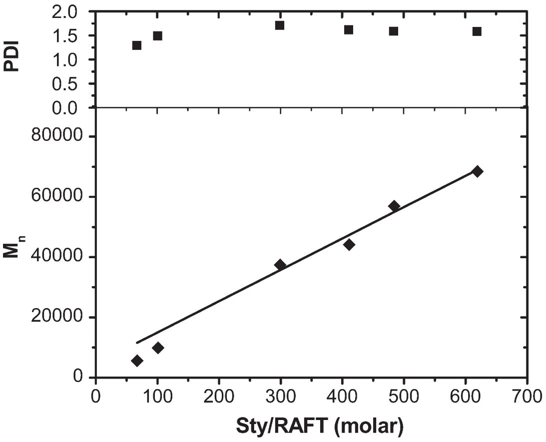

Figure 11. Comparison of experimental (◆) and theoretical (−) number-average molecular weights obtained by GPC for the final polymer formed for the range of styrene/RAFT ratios considered for the miniemulsion polymerization systems stabilized by RAFT-$Sty_{28}AA_{20}$. The polydispersities obtained for these polymers are shown in the upper part of the figure (■).

final polymer revealed no evidence of the high molecular weight polymer that such a process would yield. The final polymer molecular weight measured by GPC for the RAFT-$Sty_{28}AA_{20}$ system over a range of macro-RAFT concentrations had values close to those theoretically calculated (Figure 11). The polydispersities of the final polymer are also presented in Figure 11. Although these values are consistent with controlled polymerization, these are somewhat higher than would be expected for solution polymerization under ideal conditions. In order to understand this we consider how emulsification occurs in this system. As new droplets are formed under shear, amphiphilic RAFT agent adsorbs irreversibly from within the droplets to the newly generated interface until that interface is saturated, depleting the droplet interior of RAFT agent. Such saturated droplets should be highly stable to coalescence, so droplets continue to subdivide and shrink toward their shear-determined size as long as a sufficient reservoir of amphiphilic RAFT agent remains available within a droplet. As emulsification tends to produce a broad initial distribution of droplets, differences in the RAFT agent concentrations might be expected between individual droplets formed at different times during emulsification and thence to local differences in monomer: RAFT ratio between droplets. This would account for the higher than expected polydispersities. The variation in concentration of macro-RAFT agent is not expected to impact on the stability of the droplets provided that all droplets have a sufficient concentration of macro-RAFT agents to provide complete surface coverage.

In this approach the molecular weight of the polymer formed is directly related to particle size via the number of macro-RAFT agent stabilizers used. However, if a lower molecular weight than dictated by the control of particle size is required, further, non-surface-active, RAFT agent can be added to the system prior to emulsification. It is also possible to use stabilizing copolymers that are not also molecular weight control agents, provided that they fulfill the requirement of generating an insoluble monolayer at the surface of the droplets.

Conclusions

We have reported a new miniemulsion system in which low molecular weight, amphiphilic RAFT diblock copolymers are used at low concentrations as sole stabilizers for emulsification and latex particle formation. The emulsion droplets are stabilized by irreversible adsorption of diblock copolymer to form an insoluble monolayer of a nonlabile electrosteric stabilizer. The nonlabile coating arrests Ostwald ripening, and eliminates the need for a second hydrophobic costabilizer for the droplets. Miniemulsion polymerization anchors the macro-RAFT agent into the latex particle, yielding a stable latex with no free surfactant, and no secondary nucleation. Ideal miniemulsion polymerization, in which monomer droplet nucleation was the only mechanism for particle formation and a one-to-one transformation of monomer droplets into polymer particles was achieved when the most hydrophobic macro-RAFT agent was used as stabilizer. Molecular weight control was established and maintained throughout the reaction. At appropriate levels of stabilizer this miniemulsion process can produce low-polydispersity particle size distributions close to those obtained from conventional emulsion polymerization. Higher stabilizer concentrations lead to complex particle morphologies attributed to the irreversible adsorption of amphiphilic block copolymer.

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