Effect of Degassing on Surfactant-Free Emulsion Polymerizations of Styrene Mediated with RAFT

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Introduction. Emulsion polymerization is a unique technique to produce polymer particles on the nanoscale that are dispersed in water. It is possible to produce polymer nanoparticles with particle sizes ranging from 15 nm to 2 μm, blends and composites consisting of a broad range of polymers, and a wide variety of particle morphologies (e.g., core−shell,[1,2] salami,[3] hemisphere[4]). The synthetic versatility of this technique allows polymer materials to be made for a wide range of industrial applications, ranging from high strength coatings to biomedical devices (e.g., diagnostic kits). "Living" radical emulsion polymerization using the reversible addition−fragmentation chain transfer (RAFT) process[5−8] has not only provided a synthetic tool to produce polymer with controlled M_n and PDI[9−17] but allowed the production of complex architectures and particle morphologies (e.g., block copolymers with core−shell morphology[18]) with different mechanical properties.[19] However, the most successful synthesis of RAFT-mediated ab initio emulsion polymerization (where the surfactant above its critical micelle concentration (cmc), water, monomer, initiator and RAFT agent are added to a reaction vessel and polymerized) is through the use of low reactive RAFT agents (xanthates[12,14,19−22]). The use of high reactive RAFT agents (e.g., cumyl dithiobenzoate) gave poor control of the molecular weight distribution and the resulting latex was invariably unstable leading to a red layer consisting of monomer, RAFT agent (red in color) and possibly some oligomeric species.[23] This was overcome by using miniemulsion polymerizations,[9,24] in which monomer droplets were stabilized using both a surfactant and organic hydrophobe (e.g., hexadecane). Other methods included the use of polymeric surfactant grown in situ.[15,16]

All these techniques required the use of ionic or nonionic stabilizers to reduce the effects of coalescence or coagulation of the polymer colloids. They are also used as the nucleation sites for polymerization, for example, in the presence of surfactant, nucleation occurs in the micelles (micellar nucleation), or in the case of miniemulsions the stabilized monomer droplets are the sites of nucleation (droplet nucleation). Without the aid of stabilizers, what is generally found for styrene mixed with water is that after agitation two distinct and separate layers consisting of styrene and water rapidly form. However, based on DLVO theory alone, Pashley[25] calculated that the interaction energy, V_s, between two dodecane droplets of 300 nm in water had an energy barrier of $800kT$, suggesting that once dispersed in water the significant surface electrostatic potential of these droplets will increase the energy required for coalescence well above that for other colloidal systems and they should remain dispersed and stable. The apparent failure of the model was prescribed to the long-range hydrophobic attractive forces,[26−28] which could extend to 100 nm.[29] However, the failure of the DLVO theory to account for long-range attractive forces was previously known and the DLVO theory was shown to be applicable only for small distances (∼0.4*a*, where *a* is the radius of the particle).[30] The Lifshitz−Parsegian−Ninham (LPN) theory suggested that long-range attractive forces are derived from radiation in the microwave and infrared regions, resulting in attractions extending to 10 000 Å in pure water and 1000 Å in saltwater.[31,32] In the former case, the theory suggested that the secondary minimum was eliminated. Langmuir[33] proposed that the long-range interactions between two colloids were electrostatic in nature, and Ise and Sogami[34] calculated this by considering volume changes as particles move toward or away from each other. Interestingly, the secondary minimum was calculated to be much greater than by the LPN theory. DLVO theory can predict the short-range interactions, especially the barrier and the depth of the first minimum, and therefore should the hydrophobic droplets be dispersed in water they should resist coalescence unless influenced by gravitational forces (especially for droplet sizes greater than 300 nm).[35] The theories above suggest that formation and coalescence of droplets is controlled to a large extent by the secondary minimum. Kinetically, this barrier can be overcome through high agitation, ultrasound, homogenization and other methods. However, the real quest is to thermodynamically reduce this barrier and produce surfactant-free emulsions.

A novel but simple method to do this that produces a stable emulsion of styrene in water in the absence of any stabilizer is through the removal of dissolved gases by several freeze−pump−thaw cycles.[36] It was found that dissolved gases could influence the long-range hydrophobic interactions to inhibit droplet release from the bulk monomer.[25,35,36] Pashley and coworkers postulated that dissolved gases could prevent droplet separation due to cavitations or vapor bridges, although at present there is no theory to account for this proposal. They also carried out ab initio styrene emulsion polymerizations in the presence of surfactant (sodium dodecyl sulfate (SDS) above its cmc) at 69 °C for 2.5 h with and without degassing.[36] They found that emulsion polymerizations that were deoxygenated with nitrogen gas gave a broad particle size distribution ranging from 35 to 200 nm, whereas, the emulsion polymerizations that were evacuated gave a distribution that was much narrower with a mean diameter of 46 nm. A fluorescein dye was then added to both emulsions to test the mechanism of nucleation, either micellar or heterocoagulation (which results from the coagulation of polymer particles). As no dye was released during dialysis with water they concluded that both systems were controlled by heterocoagulation. Kühn and Tauer[37] carried out similar ab initio experiments but in the absence of surfactant, in which the reaction mixtures were evacuated at elevated temperatures. They proposed that the nucleation mechanism occurred by the cluster formation of waterborne oligomers (homogeneous nucleation).

In this communication, we report the first RAFT-mediated ab initio surfactant-free emulsion polymerizations of styrene using the novel degassing technique. The RAFT agents used were the low reactive xanthate (**1**, $CH_3(Ph)CH-SC(OEt)=S$) and the highly reactive 1-phenylethyl phenyldithioacetate ($S=C(CH_2Ph)S-CH(CH_3)Ph$) toward styrene. The xanthate has been shown to transport from the droplets to the growing phase

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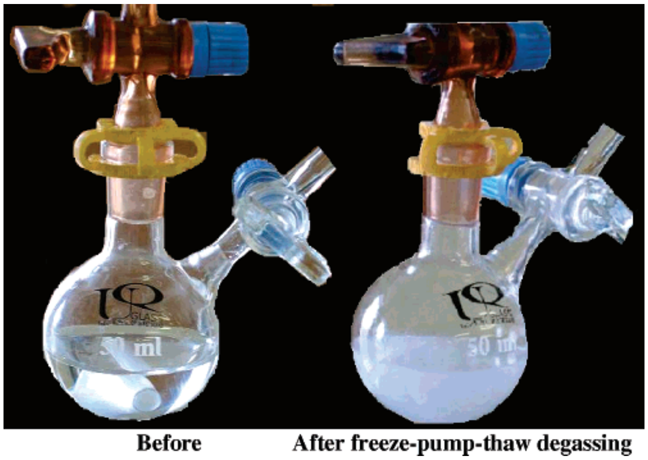

Figure 1. Photograph of the formation of a surfactant-free emulsion of styrene in water before and after three consecutive freeze−pump−thaw cycles. A turbid solution is formed after degassing, with a thin monomer layer residing on the top of the reaction mixture.

due to its slow consumption during the polymerization. On the other hand, all the high reactive 1-phenylethyl phenyldithioacetate cannot transport to the growing particles within the first few percent conversion, resulting in loss of control over the molecular weight distribution. Finally we proposed a mechanism for nucleation in surfactant-free emulsion polymerization.

Results and Discussion. The first set of styrene reactions in water with ammonium persulfate (APS) were carried out in the presence and absence of SDS and RAFT agent (**1**) and degassed by three successive freeze−pump−thaw cycles at a vacuum of less than 5×10^{-3} Torr. In all experiments the weight ratio of styrene to RAFT agent was kept constant, and a turbid solution was formed with a thin monomer layer residing on the top of the reaction after degassing (Figure 1). The mixtures were polymerized at 70 °C under magnetic stirring. The stable droplets formed by the freeze−pump−thaw method are in the size range of 2−4.7 μm for all experiments (Table 1). The conversion data given in the table ranged from 3 to 71% but were not reproducible. The reason for this is still unclear, but could be due to sampling of the reaction due to the monomer layer, or possible changes in the vacuum pressure from sample to sample. The particle diameter after 4 h of polymerization in the absence of **1** and SDS (experiment 1b) was close to 215 nm at the 3 wt % of styrene. It was found upon addition of SDS (0.0125 g, experiment 2b) the that the particle diameter decreased to approximately 140 nm. Increasing the SDS (0.025 g, experiment 3b) only slightly decreased the diameter, 122 nm. This trend is representative of experiments carried out using different weight percents of styrene. The molecular weight data also showed that as SDS was increased the M_n increased by an order of magnitude. This is possibly a result of a lower entry rate coefficient due to the increased number of particles.[38] The introduction of **1** (with no SDS, experiment 4) resulted in a particle diameter close to 200 nm. The addition of SDS below its critical micelle concentration in the presence of **1** (experiments 5 and 6) showed that the diameter decreased to about 100 nm. This is consistent with SDS stabilizing particles from coagulation, and with previous finding where the presence of **1** decreased the particle diameter and increased the number of particles.[18]

The change in M_n with conversion is given analytically using eq 1.[39] It should be noted that this equation is valid for solution and bulk experiments, but has been found to fit with ab initio experiments when low reactive xanthates are used.[10,12]

$$M_n = \frac{[M]_o x}{([RAFT]_0 - [RAFT]_0(1 - x)^{C_{tr}}) + af([I]_0 - [I]_x)} mw \qquad (1)$$

where $[M]_0$ is the initial monomer concentration, x is fractional monomer conversion to polymer, $[RAFT]_0$ is initial RAFT agent concentration, $[RAFT]_x$ is RAFT agent concentration at x, a is the mode of termination (a equals 1 for termination by combination), $[I]_0$ is initial initiator concentration, $[I]_x$ is initiator concentration at x, mw is the molecular weight of the monomer unit, f is the initiator efficiency, and C_{tr} ($=k_{tr,RAFT}/k_p$) the RAFT

Table 1. Experimental Conditions and Results for the ab Initio Emulsion Polymerization of Styrene in Water, Initiated with Ammonium Persulfate (APS) in the Presence of SDS and/or Xanthate, 1, Degassed by Three Successive Freeze−Pump−Thaw Cycles, and Polymerized at 70 °C[a]

							D (nm)				
expt	wt %	STY (g)	SDS (g)	H_2O (g)	**1** (g)	x	$t_{polym} = 0$ h	$t_{polym} = 4$ h	M_n theory (at x)	M_n	PDI
1											
a	1	0.2	0	19.8		0.3	3954	214		36 804	2
b	3	0.6	0	19.4		0.08	4207	216		39 877	1.91
c	5	1	0	19.0		0.04	4678	213		39 058	1.92
2											
a	1	0.2	0.0125	19.8		0.71		78		135 976	4.8
b	3	0.6	0.0125	19.4		0.39		140		537 910	1.9
c	5	1	0.0125	19.0		0.35		159		408 025	2.2
3											
a	1	0.2	0.025	19.8		0.34	4623	66		59 407	6.4
b	3	0.6	0.025	19.4		0.32	4404	122		238 713	3.2
c	5	1	0.025	19.0		0.08	4145	137		559 329	1.9
4											
a	1	0.2	0	19.8	0.0015	0.14	3965	190	43 733	13 193	1.9
b	3	0.6	0	19.4	0.0045	0.14	3986	203	43 807	18 599	1.9
c	5	1	0	19.0	0.0074	0.03	3424	215	44 695	21 240	1.9
5											
a	1	0.2	0.0125	19.8	0.0015	0.1	2452	60	43 584	10 096	2.1
b	3	0.6	0.0125	19.4	0.0045	0.21	1568	105	42 727	36 625	1.7
c	5	1	0.0125	19.0	0.0074	0.39	2346	137	41 724	48 546	1.8
6											
a	1	0.2	0.025	19.8	0.0015	0.3		86	41 975	23 959	1.9
b	3	0.6	0.025	19.4	0.0045	0.14		96	43 279	26 860	1.9
c	5	1	0.025	19.0	0.0074	0.09		107	44 249	41 005	2

[a] The number-average molecular weight, M_n, polydispersity index (PDI), and diameter (D) of the droplets at time zero and after 4 h of polymerization as measured by dynamic light scattering (DLS) are given. The APS used is 0.0015 g.

Table 2. Experimental Conditions and Results for the ab Initio Emulsion Polymerization of Styrene in Water, Initiated with Ammonium Persulfate (APS) in the Presence of Hexadecane and/or Xanthate, 1, Degassed by Three Successive Freeze−Pump−Thaw Cycles, and Polymerized at 70 °C

							D (nm)				
expt	wt %	STY (g)	H_2O (g)	**1** (g)	hexadecane (g)	*x*	$t_{polym} = 0$ h	$t_{polym} = 4$ h	M_n theory (at *x*)	M_n	PDI
7											
a	1	0.2	19.8	0	0.0039	0.33	191	232		156 805	3.22
b	3	0.6	19.4	0	0.0118	0.1	108	199		66 792	2.24
c	5	1	19	0	0.0196	0.05	80	196		75 671	2.01
8											
a	1	0.2	19.8	0.0015	0.0039	0.16	197	142	43 124	9657	2.23
b	3	0.6	19.4	0.0045	0.0118	0.09	141	186	43 659	21 624	2.12
c	5	1	19	0.0074	0.0196	0.1	230	190	44 173	26 729	2.02
9[a]	3	0.6	19.4	0.0045	0.0118	0.14	220	165	2712	2023 (34 799)[b]	1.17 (2.04)[b]

[a] Experiment 9 was carried out using the highly reactive RAFT agent 1-phenylethyl phenyldithioacetate. [b] The SEC showed a biomodal distribution for experiment 9. The M_n and PDI in brackets are for the second higher molecular weight peak. [c] The number-average molecular weight, M_n, polydispersity index, and diameter (*D*) of the droplets at time zero and after 4 h of polymerization as measured by dynamic light scattering (DLS) are given. Experiment 9 was carried out using the highly reactive RAFT agent 1-phenylethyl phenyldithioacetate instead of **1**. The APS used is 0.0015 g.

chain transfer rate constant. For example, using a RAFT agent with a C_{tr} value of 1 will give an M_n that is constant (at its maximum value) over the conversion range (see ref 39 for more details).

The M_n values without SDS (experiment 4) were much less than that of theory (eq 1), using a C_{tr} value of 0.68 for this RAFT agent.[40] The M_n values at 5 wt % of STY (experiments 5c and 6c) were close to theory upon the addition of SDS. However, at lower wt % of STY, the M_n was much lower than theory., and the reason for this is still unclear, as previous work showed that there was a good fit between theory and experiment.[18] The PDI of all reactions in the presence of **1** were close to 2, consistent with other work.[18] Although the results demonstrated that the freeze−pump−thaw method produced droplets in the absence of any stabilizer, the mechanism of nucleation and thus particle formation for this system is more complex to elucidate. The data suggests that nucleation is primarily through homogeneous nucleation, in which the small oligomers (above its critical chain length, *j*, are no longer soluble in the aqueous phase) coagulated to form particles. The droplets formed from the freeze−pump−thaw method will coalesce and then finally rise and join the top monomer layer,[25] and the remaining droplets only provide a means of supplying monomer to the growing particles. This is in accord with the slow rate of polymerization and the particle diameter found by Tauer et al.[41,42] for surfactant-free emulsion polymerizations of styrene. In the presence of **1**, the M_n was in most cases lower than theory, suggesting that **1** could transport from the droplets at a fast rate to the growing particles to control the molecular weight distribution. This is supported from the size exclusion chromatography (SEC) data (see supporting material) that showed the S=C(OEt)−S moiety (has a strong absorbance at 300 nm) is attached to most polymer chain ends. The use of a highly reactive RAFT agent ($S{=}C(CH_2Ph)S{-}CH(CH_3)Ph$, 1-phenylethyl phenyldithioacetate) showed little or no control in M_n with very high PDIs (results not shown), presumably due to its poor transportation to the growing particles.[23]

Unfortunately, we have provided evidence that the styrene droplets did not act as nucleation sites but served only as a monomer reservoir. We then decided to add hexadecane in the absence of SDS to stabilize the droplets from Oswald ripening reducing droplet coalescence, and thus maintain a high droplet number. This should in principle allow droplet nucleation to be a competing process similar to conventional miniemulsion.[43] Table 2 shows the results for the freeze−pump−thaw method used to produce an emulsion in the presence of hexadecane (which was kept at the same ratio to styrene for all experiments), after which polymerization was carried out at 70 °C for 4 h. In these experiments, the initial droplet diameter (at $t_{poly} = 0$ h) was between 100 and 200 nm, sizes that are an order of magnitude lower than in the absence of hexadecane (e.g., experiment 1). This indicated that droplet formation and/or droplet stability was influenced by the presence of hexadecane. In the absence of **1** (experiment 7), the particle diameter was close to 200 nm (only slightly greater than the initial droplet sizes), the M_n values after 4 h of polymerization were much higher than values found in experiment 1, and the PDI is greater than 2. In the presence of **1** (experiment 8), the particle diameters ranged from 140 to 190 nm and smaller than their respective initial droplet sizes, the M_n was lower than theory, and PDI is close to 2. This shows that the polymerizations in the presence of hexadecane were controlled by **1**, but once again the reason for the lower M_n values is unclear. The data in Table 2 illustrates that nucleation could be via both homogeneous and droplet nucleation (see Scheme 1 in Supporting Information). However, it is difficult to separate the dominant process. To do this we added the highly reactive 1-phenylethyl phenyldithioacetate, in which a linear increase in M_n vs conversion and a low PDI (below 1.1) should be observed. Experiment 9 (3 wt % of styrene) in Table 2 shows that the particle diameter decreased to 165 nm from the initial droplet size of 220 nm. The molecular weight distribution was bimodal (Figure 2), in which the low molecular weight peak had an M_n of 2023 and PDI of 1.17, and the second (higher) molecular weight peak had an M_n of

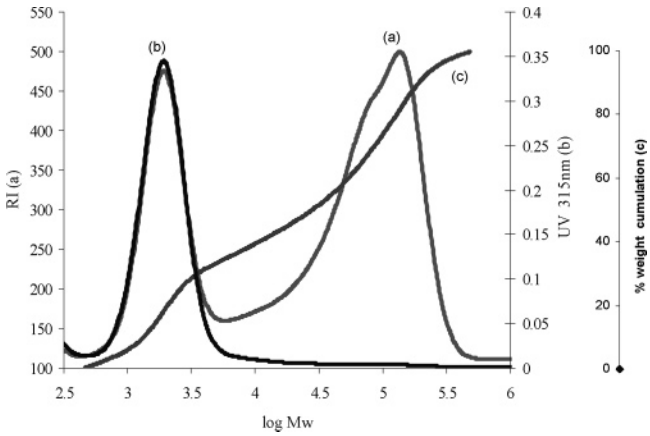

Figure 2. Size exclusion chromatography (SEC) of ab initio emulsion polymerization of styrene in water, hexadecane, ammonium persulfate (APS) and 1-phenylethyl phenyldithioacetate at 70 °C after three freeze−pump−thaw cycles (experiment 9). Key: (a) RI detection of the polymer after 4 h polymerization, (b) UV detection at 315 nm (for detection of only $S{=}C(CH_2Ph)S{-}$ moiety), and (c) % cumulative weight fraction of polymer as determined from the weight distribution from RI detection.

34 800 and PDI of 2.04. Evaluating the molecular weight distribution at 315 nm allowed us to determine the distribution of polymer chains with S═C(CH2Ph)S− moieties. Figure 2b shows that these RAFT moieties were only attached to polymer chains in the first low molecular weight peak ($M_n = 2023$) and not to the second high molecular weight peak. This result provides insight into the mechanism of particle formation in the presence of hexadecane. The data supports the postulate that the droplets stabilized by hexadecane contain the same ratio of styrene to 1-phenylethyl phenyldithioacetate as the initial starting ratio. These droplets are then nucleated and the polymer chains grow in a "living" fashion (i.e., producing a polymer with a very low PDI (1.17)) with a very low M_n, which is consistent with theoretical calculations at this conversion. In addition to droplet nucleation there was a considerable amount of polymer formed through homogeneous nucleation. It is also clear from the two very separate molecular weight distributions that there is little heterocoagulation between particles containing polymer with RAFT end groups and those without. The weight distribution of the SEC shows that the first peak contains 35 wt % of the polymer and the second peak 65 wt %. However, based on a number distribution it is calculated that over 80% of polymer chains have RAFT end groups.

Conclusion. The effect of degassing through successive freeze−pump−thaw cycles provides a novel route to the formation of a styrene−water emulsion. This emulsion was then polymerized with APS in the absence of SDS and it was found that particle diameter was an order of magnitude lower than the initial droplet size. The addition of SDS below the cmc had little influence to stabilize the droplets. The addition of RAFT agent, **1**, also did not affect the initial droplet size but did allow for a controlled molecular weight that was close to theory. The novelty of this work was to reduce the droplet size by the addition of hexadecane (in the absence of SDS) to stabilize the droplets against Oswald ripening. The droplet size decreased by an order of magnitude and was similar to the polymer particles after polymerization. In this case, the molecular weight distribution using **1** was in most cases below theory. The use of the highly reactive RAFT agent, 1-phenylethyl phenyldithioacetate, also gave similar droplet and particle sizes. However, the molecular weight was composed of two distinct peaks, the first low molecular weight peak corresponding to particles containing poly-RAFT formed through droplet nucleation, and the second higher molecular weight peak corresponding to particles without poly-RAFT. On the basis of the number distribution, the percentage of polymer with RAFT end groups was 80%.

Although there is no theory to account for long-range hydrophobic interactions through degassing, we believe that the degassing process can reduce the secondary minimum sufficiently to obtain a stable emulsion with a thin monomer layer residing on the top. More work is required to fully elucidate this mechanism, and perhaps a higher vacuum would allow us to approach a system with a sufficient number of droplets to significantly reduce or eliminate homogeneous nucleation. Applying the degassing technique to emulsion polymerization opens a new and exciting area of polymer synthesis and polymer colloidal properties.

Supporting Information Available: Text giving experimental and charaterization details and figures showing size exclusion chromatography and the TEM of polystyrene particles. This material is available free of charge via the Internet at http://pubs.acs.org.

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