Nitroxide-Mediated Styrene Surfactant-Free Emulsion Polymerization

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Introduction. Living/controlled radical polymerization (L/CRP) provides a facile route to the syntheses of polymers with complex microstructure and narrow molecular weight distributions, once the domain of living ionic polymerizations. The three techniques appearing most frequently in the literature are: reverse addition fragmentation chain transfer polymerization,[1] atom transfer radical polymerization,[2,3] and stable free radical polymerization (SFRP).[4] Irreversible termination reactions do occur in L/CRP, but the benefits include mild reaction conditions and a tolerance to impurities, including water, which is advantageous because it allows for aqueous based polymerizations.[5,6] Research in heterogeneous SFRP has focused primarily on two nitroxides; 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) and *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1). TEMPO is generally restricted to polymerization of styrenics above 120 °C, while SG1 is more versatile with the ability to control acrylates and styrenics[7] at temperatures as low as 90 °C.

The original attempts to conduct a nitroxide-mediated emulsion polymerization generally suffered from poor latex stability leading to severe coagulum formation,[8,9] probably due to the method of particle nucleation and the partitioning of various species in the system. Adopting a miniemulsion approach allowed for a controlled polymerization in colloidally stable systems, and provided insight into the challenges associated with conducting heterogeneous SFRP.[5,10,11] Nevertheless, the ability to conduct SFRP in an emulsion is desirable because it simplifies the formulation by removing the need for a hydrophobe (which has to be removed from the final product) and the application of high shear to form the initial emulsion. Szkurhan and Georges[9] successfully developed an SFRP emulsion process that bypasses the particle nucleation steps using a nanoprecipitation technique consisting of TEMPO-terminated oligomers of polystyrene in monomer-swollen particles. Considerable progress has also been made by Charleux et al.[12−15] in developing an SFRP emulsion process using an SG1-based water-soluble alkoxyamine. The multistep emulsion polymerization starts with a surfactant solution (under microemulsion-like conditions) that is initiated with a variety of water-soluble SG1 compounds to form a seed latex (particle size 150−200 nm), followed by a one-shot monomer addition to complete the polymerization. The process is capable of synthesizing well-controlled polymers of poly(*n*-butyl acrylate) and polystyrene, as well as diblock and triblock copolymers.

A surfactant-free emulsion polymerization has also been reported by first synthesizing a SG1-terminated poly(sodium acrylate) in a 1,4-dioxane solution which is than used as a water-soluble macroinitiator.[16,17] The batch process allowed for the synthesis of amphiphilic diblock copolymers of both styrene and butyl acrylate that formed nanoparticles stabilized by the hydroplilic poly(acrylic acid)-based shell. The molecular weight was higher than the theoretical molecular weight, the result of low initiator efficiency and significant radical−radical termination early in the polymerization, making the technique inadequate for the synthesis low molecular weigh polymers (M_n < 20 000 g·mol^{-1}) with a high degree of livingness.

Herein, we report the two-stage nitroxide-mediated surfactant-free polymerization of styrene mediated with SG1 and initiated by the thermal decomposition of the water-soluble initiator potassium persulfate (KPS), which eliminates the need to synthesize a macroinitiator. The sulfate end group on the polymer chain provide the stability for the latex. The molecular weight grows with conversion and is in agreement with the theoretical molecular weight. Low molecular weight (M_n < 20 000 g·mol^{-1}) homopolymers of polystyrene with a high degree of livingness (shown by successful chain extension with butyl acrylate) can be targeted and easily synthesized.

Experimental Section. Materials. Potassium persulfate (Aldrich, >99%), styrene (Aldrich, >99%), *n*-butyl acrylate (Aldrich, >99%), sodium bicarbonate ($NaHCO_3$, Aldrich, >99.5%), and potassium carbonate (K_2CO_3, Aldrich, 99%), SG1 (supplied by Arkema, 89%) were all used as received.

Emulsion Polymerization. SG1 (0.126 g, 4.27×10^{-4} mol) was added to 1.5 g (1.4×10^{-2} mol) of styrene and stirred for 10 min. The solution was transferred to a 250 mL round-bottom flask fitted with a condenser, containing KPS (0.068 g, 2.5×10^{-4} mol) and K_2CO_3 (0.026 g, 1.9×10^{-4} mol) dissolved in deionized water (90 g). The system was purged with ultrahigh-purity nitrogen for 30 min before being immersed in a 90 °C oil bath with the magnetic stirring speed set to 650 rpm. After 3.5 h elapsed an additional 8.5 g (8.2×10^{-2} mol) of deoxygenated styrene was added over 10 min. Samples were withdrawn with a deoxygenated syringe and placed in an ice bath.

Chain Extension. At the completion of the emulsion polymerization the polymer was precipitated in methanol, filtered, washed, and dried under vacuum overnight (M_n = 16 178 g·mol^{-1}, PDI = 1.77). The SG1-terminated polymer was dissolved in butyl acrylate (~50 g, 0.39 mol) in a 100 mL round-bottom flask fitted with a condenser. The system was purged with ultrahigh-purity nitrogen for 30 min before being immersed in a 90 °C oil bath with the magnetic stirring speed set to 300 rpm. After 2.5 h the flask was removed from the oil bath and the solution cooled to room-temperature prior to a sample taken.

Characterization. After the polymerizations were complete the latexes were filtered (Fisherbrand P8 creped) to collect any coagulum. The amount of coagulum was determined gravimetrically. Monomer conversions were determined gravimetrically. Size exclusion chromatography (SEC) was used to measure the molecular weight distribution of the polymer samples. The SEC was equipped with a Waters 2960 separation module containing four Styragel columns (100, 500, 10^3, 10^4 Å) maintained at 40 °C, coupled with a Waters 410 differential refractive index (RI) detector. Tetrahydrofuran (THF) was used as the eluant and the flow rate was set to 1 mL·min^{-1}. The RI detector was calibrated with narrowly distributed polystyrene standards ranging from 347 to 355 000 g·mol^{-1}. The particle size was measured using a Matec Applied Sciences Capillary Hydrodynamic Fractionation (CHDF) 2000 unit. The UV

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detector was set to 220 nm. The eluant was a 20:1 mixture of deionized water/GR500-1X (Matec Applied Sciences). Samples were diluted with the eluant to approximately 3.5 wt % solids and sonicated for 5 min. Samples were passed through a 0.5 μm pore size filter prior to injection. The marker was a 2 wt % solution of sodium benzoate. To ensure that there were no particles greater than 0.5 μm the particle size distributions were also measured using a Malvern Mastersizer 2000 equipped with a Hydro 2000S optical unit. The refractive index value for water and polystyrene were 1.33 and 1.56, respectively.

Results and Discussion. A water-soluble alkoxyamine is formed by the thermal decomposition of KPS to sulfate radicals (and hydroxide radicals)[18] that propagate with the styrene dissolved in the aqueous phase, adding 1−2 styrene units before reversible termination by SG1.[9,19] The bicomponent (KPS and SG1) system leads to an induction period that continues until the concentration of free SG1 is low enough to allow for a reasonable rate of chain growth of the alkoxyamine species. Monomer addition reduces the water solubility of the alkoxyamine, leading to surfactant-like behavior of the species (i.e., the species are expected reside at the organic/aqueous interface as well as form micelles). Once the number of styrene units exceeds a critical length, the chain will be rendered too hydrophobic to desorb into the aqueous phase.

Initial experiments were simple batch emulsion processes that resulted in poorly controlled polymerizations and unstable latexes. To stimulate the creation of micelles, the desired loci of polymerization, a multistage approach was adopted starting from dilute styrene/water solutions to favor the formation of the alkoxyamine and short chain SG1-oligomers (stage one) before the addition of the majority of the styrene (stage two). A series of experiments lead to the formulation described in the experimental section that produced the well-controlled polymerization illustrated in Figure 1. The particle distribution was monomodal and the weight-average particle diameter was 121 ± 21 nm, with ~5 wt % coagulum at the end of the polymerization. The particle sizes were confirmed with a Malvern Mastersizer 2000, which also demonstrated the absence of large particles in the system.

The conversion vs time plot shown in Figure 1a shows an induction period of ~3.5 h, where little conversion occurs. This corresponds to the first stage of the polymerization where 1.5 g of styrene ($[\mathrm{SG1}]_0/[\mathrm{KPS}]_0 = 1.5$; $[\mathrm{styrene}]_0/[\mathrm{SG1}]_0 = 38$) is dispersed in 90 g of water, and the dominant product is SG1-terminated oligomers (with less than 5 styrene units based on SEC analysis) with primarily sulfate end groups. The polymerization proceeded rapidly after the addition of 8.5 g of styrene (stage two) at the 3.5 h mark of the polymerization. The duration of the first stage corresponds roughly to the time required for the complete thermal decomposition of KPS at 90 °C.[18] A decrease in the allotted time for stage one resulted in poor behavior of the polymerization and an unstable latex. Similarly, increasing the duration of the first stage to 8 h had detrimental effects on the system. After 3.5 h the conversion (of the 1.5 g of styrene) was less than 15%, but an additional 5.5 h of reaction time yielded no further conversion. When stage one was run for 8 h the second stage of the polymerization proceed very slowly, with a significantly higher number-average molecular weight (M_n), indicating that polymer chains were irreversibly terminated during the extended time of stage one.

Given the low conversion at the end of stage one, and that Szkurhan and Georges[9] were able to produce TEMPO-terminated styrene oligomers (with 1−2 units) from a styrene-saturated aqueous solution of KPS and TEMPO, the effect of the $[\mathrm{styrene}]_0/[\mathrm{SG1}]_0$ ratio was investigated. Attempts were made at reducing the amount of styrene to ~0.2 g ($[\mathrm{styrene}]_0/[\mathrm{SG1}]_0 = 5$) which would saturate the aqueous phase with styrene but limit the presence of styrene droplets. This adversely affected the formation of the SG1-terminated oligomers and the polymerization, which proceeded slowly (or not at all) and produced high M_n (>20 000 g·mol^{-1}) polymers at less than 10% conversion with significant coagulum formation. The situation was not improved by increasing the styrene content to 0.75 g ($[\mathrm{styrene}]_0/[\mathrm{SG1}]_0 = 19$), indicating that the excess styrene (forming monomer droplets in the system) may contribute to the successful formation of SG1-terminated oligomers. The process developed by Farcet et al.[19] used the KPS−SG1 bicomponent system to effectively initiate a nitroxide-mediated styrene miniemulsion (i.e., in the presence of excess styrene).

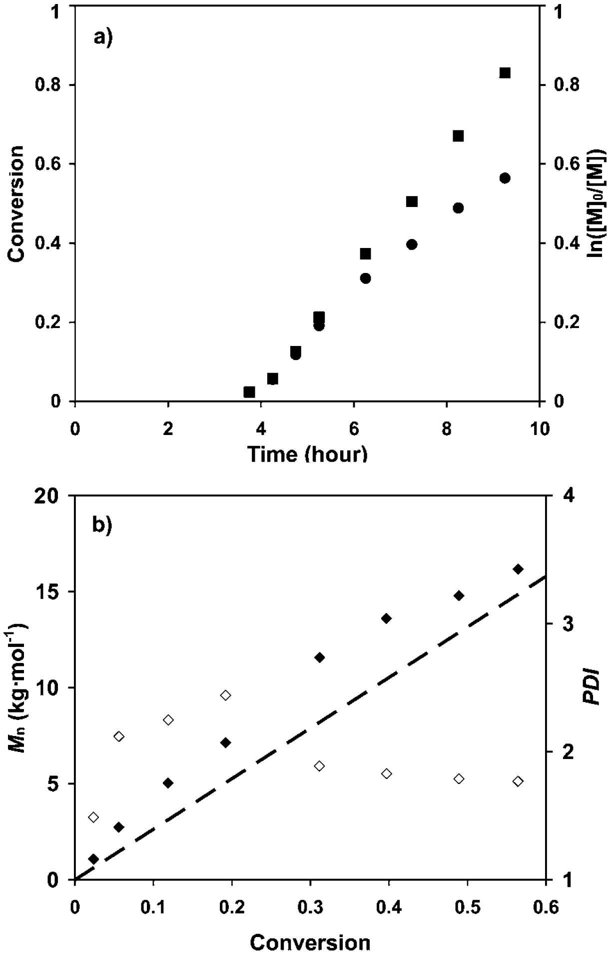

Figure 1. (a) Conversion vs time (●) and kinetic plots (■) and (b) evolution of number-average molecular weight (M_n, ◆) and polydispersity index (PDI, ◇) with conversion for the potassium persulfate (KPS) initiated, surfactant-free emulsion, *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) mediated polymerization of styrene 90 °C. 10 wt % styrene content; n(KPS) = 2.52×10^{-4} mol; n(SG1) = 4.27×10^{-4} mol; $n(\mathrm{K_2CO_3}) = 1.91 \times 10^{-4}$ mol; dashed line represents the theoretical M_n based on SG1 ($M_{n,\mathrm{theory}}$ = conversion × $[\mathrm{styrene}]_0/[\mathrm{SG1}]_0$).

Figure 1b shows that the M_n increased with monomer conversion, however the polydispersity index (PDI) remained somewhat high for the duration of the polymerization. The PDI increases with conversion reaching a value of 2.44 at ~20% conversion before steadily decreasing to a final value of 1.77. (By comparison, typical PDI values for well-behaved SG1-mediated styrene (mini)emulsions are ~1.5.[16]) A large PDI does

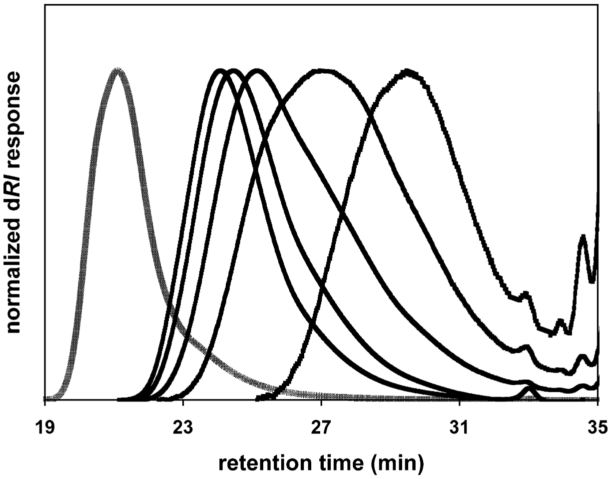

Figure 2. SEC traces for the surfactant-free emulsion polymerization of styrene mediated with SG1. See Figure 1 for conditions. Conversion increases from right to left; conversion = 3%, M_n = 1070, PDI = 1.49; conversion = 6%, M_n = 2750, PDI = 2.12; conversion = 12%, M_n = 5040, PDI = 2.25; conversion = 31%, M_n = 11 580, PDI = 1.89 conversion = 56%, M_n = 16 180, PDI = 1.77; (gray line) chain extension with butyl acrylate.

not negate the living nature of polymerization, as evidenced from the evolution of the entire molecular weight distributions with monomer conversion and the chain extension to form a polystyrene-*b*-poly(butyl acrylate) copolymer (Figure 2). Although polymer chains are initiated over a span of hours, the bicomponent system ensures that propagation begins only after most of the chains have been formed. With the majority of chains formed at a monomer conversion less than 3% the long initiation period cannot solely account for the broad distribution of the polymer. A contributing factor to the large PDI is the heterogeneity of the system. When the styrene is introduced in the second stage of the polymerization the resulting emulsion contains monomer-swollen micelles and droplets of various sizes (up to microns in diameter), stabilized by the sulfate end group of the surfactant-like SG1-oligomers. After several activation/deactivation cycles the polymer chains are no longer water-soluble, and are tethered to the particle surface by the sulfate end group. Consequently, the number (or concentration) of polymer chains in a particle is a function of the surface area of the particle, while the amount of free SG1 (assumed to rapidly establish phase equilibrium)[19,20] is dependent on the volume of the particle. Hence, the [chains]/[SG1] ratio, responsible for the polymerization rate and degree of control over the polymerization, is a function of the particle's size, and it is this effect that is believed to contribute to the large PDI. It is believed that the living polymer chains have different propagation rates depending on the size of the particle. During the development of this system, failed experiments consistently had both broad (and usually bimodal) particle distributions with broad monomodal molecular weight distribution at low conversion that grew into bimodal (or developed a distinct shoulder) molecular weight distributions as the polymerization proceeded. The importance of a uniform particle size in providing an identical environment in aqueous based nitroxide-mediated polymerizations is further highlighted by the confirmation of compartmentalization effects and its influence over the propagation rate and control in aqueous based SFRP, with smaller particles resulting in lower rates of polymerization and significantly higher chain livingness.[21−24]

The ability to conduct living polymerizations of styrene at 90 °C mediated with SG1 is a consequence of its relatively high dissociation rate constant[7] and its inherent instability in water, which is accelerated at lower pH.[19] The thermal decomposition of KPS produces sulfate radicals that add to a styrene unit or react with water to form HSO_4^- and $HO^\bullet$.[18] When the system was not buffered (final pH ~2.8) the polymerizations were uncontrolled presumably because of the low concentration of SG1, which readily decomposes at low pH.[19] The addition of 1.91×10^{-4} mol of K_2CO_3 ($[KPS]_0/[K_2CO_3]_0 = 1.32$) produced a latex with a final pH of ~6.1 and the polymerization was well controlled, while excess K_2CO_3 ($[KPS]_0/[K_2CO_3]_0 = 1.05$, final pH ~8.3) limited the polymer conversion to less than 10%, attributed to the buildup of SG1 that is stable at higher pH. The use of $NaHCO_3$ as a buffer was also investigated, requiring approximately twice the loading of K_2CO_3 to achieve a comparable final pH of the latex. While the progress of the polymerization was similar to that of the K_2CO_3 buffered experiment, the poor colloidal stability and significant coagulum formation was attributed to the additional electrolyte that reduced the effectiveness of the stabilizing sulfate end groups.

Conclusions. A two-stage nitroxide-mediated surfactant-free emulsion polymerization of styrene was successfully carried out using the water-soluble initiator KPS and the nitroxide SG1. An initial ratio of SG1:KPS of 1.5 was required to produce a well-controlled polymerization, provided that the pH of the latex (latex buffered with K_2CO_3) was approximately 6. An excess amount of K_2CO_3 caused the pH of the latex to remain above 8 and no polymerization occurred, while a lack of K_2CO_3 resulted in a low pH that produced poorly controlled polymerization. The heterogeneity in the particle size leads to increased PDI, but control is shown by the increase in M_n with conversion, the evolution on the entire molecular weight distribution with conversion, and successful chain extension with butyl acrylate.

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