Macromolecules **2002,** *35,* 6915−6919

Surfactant Concentration Effects on Nitroxide-Mediated Living Free Radical Miniemulsion Polymerization of Styrene

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Received April 17, 2002; Revised Manuscript Received July 3, 2002

ABSTRACT: TEMPO-terminated oligomers of polystyrene (TTOPS) are being used as a macroinitiator to initiate the miniemulsion polymerization of styrene at 125 °C. In this work, the surfactant concentration (Dowfax 8390) used to prepare the miniemulsion was varied from 1.25 to 25 mM. It was found that with increasing surfactant concentration the particle size decreased, and the particle number increased as expected. However, this variation in the surfactant concentration and its effect on the number of particles generated had little effect on the resulting polymerization rate and polymer molecular weight in the nitroxide-mediated miniemulsion system. The average numbers of active and stable free radicals per particle were estimated and used to explain the kinetic differences between living free radical miniemulsion polymerization and normal free radical emulsion polymerization.

Introduction

Controlled/“living” free radical polymerization is a relatively new and simple route to the synthesis of polymers and/or copolymers with controlled molecular weights having narrow distributions, desired architectures, and end groups. Living free radical polymerization is usually divided into three categories on the basis of the different controlling mechanisms.[1,2] Stable free radical polymerization (SFRP) is the most frequently applied method of living free radical polymerization.[3−6] Since nitroxide radicals are most often used as the stable free radical to control the polymerization, sometimes it is referred to as nitroxide-mediated polymerization (NMP).[7,8] Atom transfer radical polymerization (ATRP)[9,10] has a similar mechanism but uses transition metal complexes instead of stable free radicals. Both methods gain control of the polymerization based on a reversible termination process. In contrast, the third category, reversible addition fragmentation chain transfer polymerization (RAFT),[11,12] differs in the mechanism by using a reversible chain transfer process. In all cases, polymer chains are built up simultaneously and grow in an activation/deactivation cycle. Only a very small fraction of chains are concurrently active (i.e., as a free radical capable of propagation, termination, etc.).

Living radical polymerizations have been predominantly studied in homogeneous systems, that is, bulk or solution polymerizations. Because of the needs of commercialization of the living free radical polymerization process, a considerable amount of effort has been directed to the development of nitroxide-mediated polymerizations under heterogeneous conditions such as suspension, dispersion, seeded emulsion, and miniemulsion.[13−19] In emulsion and miniemulsion polymerizations, surfactant is one of the most crucial ingredients. In conventional emulsion and miniemulsion polymerizations, the surfactant concentration is directly related to the latex particle size and stability. By controlling the particle size and particle number in emulsion and miniemulsion systems, the surfactant concentration is used to control the polymerization rate and molecular weight.

Nitroxide radical (most often 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO)) controlled miniemulsion polymerizations of styrene are most commonly used in these studies.[15−19] Some kinetics features of nitroxide-mediated miniemulsion polymerizations of styrene are significantly different from conventional emulsion or miniemulsion polymerizations of styrene. For example, in a conventional emulsion or miniemulsion polymerization of styrene, the average number of active radicals per particle, $\bar{n}$, is typically close to 0.5. However, $\bar{n}$ is found to be low, in the range of 0.001−0.01, in nitroxide-mediated systems.[18,19] This is classified by Smith and Ewart[20] as case 1 kinetics ($\bar{n} \ll 0.5$). In conventional free radical emulsion polymerizations, this is attributed to a high escape rate of radicals from the particles. Low $\bar{n}$ values (~0.02, which is about an order of magnitude larger than the corresponding miniemulsion polymerization of styrene initiated with TTOPS) were also found in the auto-polymerization of styrene miniemulsions (thermally self-initiated),[18] which is caused by the slow radical generation rate and significant desorption of radicals resulting from chain transfer to monomer. This explanation is not applicable, however, in nitroxide-mediated miniemulsion polymerizations of styrene. The relationship between particle number and polymerization rate and molecular weight (i.e., an increasing number of particles results in an increasing polymerization rate and higher molecular weights) is based on the assumption of Smith−Ewart case 2 kinetics ($\bar{n} = 0.5$). When $\bar{n} \ll 0.5$, the relationship may be different. Therefore, it is important to study the effect of surfactant in these systems. This paper will focus on the study of the effects of surfactant concentration on nitroxide-mediated miniemulsion polymerizations initiated by TEMPO-terminated oligomers of polystyrene (TTOPS).

Experimental Section

Materials. Styrene (Aldrich) monomer was cleaned before use by distillation, while the remaining reagents were used as received. Dowfax 8390 (disulfonated alkyl diphenyl oxide sodium salt; Dow Chemical Co.), an anionic surface-active

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10.1021/ma0206016 CCC: $22.00

Table 1. Recipe for Living Free Radical Miniemulsion Polymerization at 125 °C[a]

ingredient	weight (g)	concentration
	Water Phase	
deionized water	97.5	
Dowfax 8390	varied	1.25–25 mM[b]
	Oil Phase	
styrene	24.4	
hexadecane	0.73	3 wt %[c]
TTOPS 1500	0.61	2.5 wt %[c]

[a] Total final solids ~20% (based on 100% conversion). [b] Based on water phase. [c] Based on the styrene monomer.

agent, was used as the emulsifier. Hexadecane (Aldrich) was used as the costabilizer. The TEMPO-terminated oligomers of polystyrene (TTOPS) were prepared by bulk polymerization of styrene and used as initiator in miniemulsion polymerization.

Preparation of TTOPS. TEMPO-terminated oligomers of polystyrene (TTOPS) were used as the initiation system in the miniemulsion polymerization. The primary reason for using TTOPS as initiator instead of TEMPO/BPO is to simplify the system. By using TTOPS as the initiator, the initial number of chains can be specified, and the expected molecular weights of these are readily estimated. In addition, TEMPO partitions between the water and monomer phases in the TEMPO/BPO system, while TTOPS will be restricted to the monomer droplet phase, as it has no water solubility. TTOPS was prepared by the bulk polymerization of styrene in the presence of benzoyl peroxide (BPO) (0.05 mol/L) and TEMPO (0.105 mol/L). The molar ratio of TEMPO to BPO was 2.1/1. The styrene was freshly distilled and degassed via several freeze–thaw cycles. In this polymerization process, the solution was preheated for 3.5 h at 95 °C to ensure complete decomposition of BPO, while no appreciable polymerization occurred because of the presence of TEMPO radicals. The system was then heated at 125 °C for 6 h. The polymer, recovered as a precipitate using a large excess of methanol, was purified by reprecipitation from a toluene (solvent)/methanol (nonsolvent) mixture. The yield was 17%, and the number-average molecular weight was 1500 g/mol, with M_w/M_n (polydispersity index) equal to 1.14 (molecular weight obtained by gel permeation chromatography (GPC), Waters Styragel columns HR3, HR4, and HR6 (35 °C), Waters 410 differential refractometer detector).

Polymerization Procedure. The recipe for the miniemulsion polymerization is shown in Table 1. TTOPS and hexadecane were predissolved in the styrene prior to emulsification. To prepare the miniemulsion, the oil and water phases were mixed and then sonified with stirring using a Branson sonifier (model 450) at a power output setting of 8 and a duty cycle of 50% for 1 min followed by passing it 10 times through the microfluidizer (model 110T, Microfluidics). After purging the miniemulsion with nitrogen (zero grade, AirGas) for 5–10 min, the polymerization was carried out in a high-pressure polymerization bottle in an oil bath operated at a controlled temperature of 125 ± 5 °C. The polymerization mixture was stirred with a magnetic bar at 500 rpm. Samples were removed from the bottle for analysis using a needle and syringe. The conversions were measured gravimetrically and confirmed by gas chromatography (HP 5890A). Molecular weight and molecular weight distributions were measured by gel permeation chromatography. Particle size distributions of the latexes were measured by capillary hydrodynamic fractionation (CHDF, MATEC Applied Sciences, model 1100) and confirmed by transmission electron microscopy (TEM, Phillips 400).

Results and Discussion

In normal free radical emulsion or miniemulsion polymerizations, an increasing surfactant concentration increases the number of particles since more surfactant molecules are available to stabilize more and smaller particles/droplets. A greater number of miniemulsion droplets results in a greater number of particles (i.e., more polymerization loci). The polymerization rate, therefore, is proportional to the number of particles, as shown in eq 1. Therefore, a higher polymerization rate is expected using a higher surfactant concentration. The rate of polymerization is given by the familiar expression

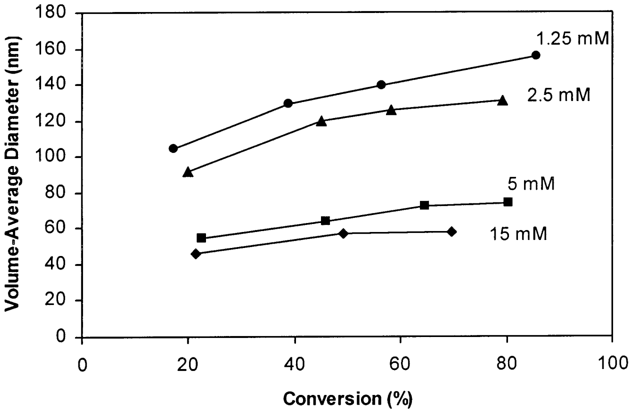

Figure 1. Evolution of volume-average particle size with conversion in living free radical miniemulsion polymerizations of styrene; 3 wt % hexadecane based on monomer; 2.5 wt % TTOPS-1500; T_r = 125 °C.

$$R_p = \frac{k_p[M]_p\bar{n}N_p}{N_A} \tag{1}$$

where k_p is the propagation rate constant, $[M]_p$ is the monomer concentration in the particles, $\bar{n}$ is the average number of free radicals per particle, N_p is the number of particles, and N_A is Avogadro's number. If the initiation rate is constant while the number of particles increases, the interval between the entry of successive radicals into a particle is lengthened. In the zero-one mechanism of emulsion polymerization, active free radicals keep adding monomer units to the polymer chains until the next radical enters and termination occurs. Hence, the molecular weight will increase with increasing particle number. For a given system, the polymerization rate is controlled by the number of particles, and the molecular weight is controlled by the interval between radical entry events. However, as found previously, the kinetics behavior of TTOPS-initiated miniemulsion polymerizations of styrene deviates from normal free radical miniemulsion polymerization,[18] and this analysis may not be valid in this system as stated in the Introduction.

The effects of different surfactant concentrations on the TTOPS-initiated miniemulsion polymerization of styrene were studied here. The hexadecane concentration used in this study was 3 wt % based on monomer. The Dowfax 8390 concentration was varied from 1.25 mM, which is below the cmc (cmc = 1.6 mM), to 25 mM. Stable latexes were obtained after 24 h polymerization at 125 °C except for the lowest surfactant concentration (1.25 mM), which contained less than 5% coagulum in the final latex.

The evolution of the volume-average particle size with conversion was measured by CHDF, and the results are shown in Figure 1. Figure 2 shows the evolution of particle number with conversion. With increasing conversion, the particle size increased. At the same time, the particle number increased with conversion. The higher surfactant concentration gave a more significant

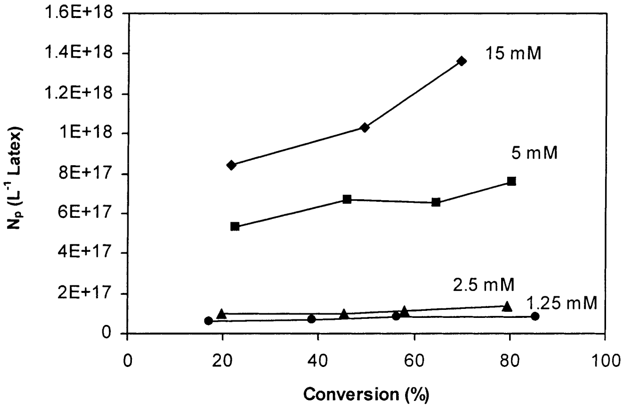

Figure 2. Evolution of number of particles with conversion in living free radical miniemulsion polymerizations of styrene; 3 wt % hexadecane based on monomer; 2.5 wt % TTOPS-1500; T_r = 125 °C.

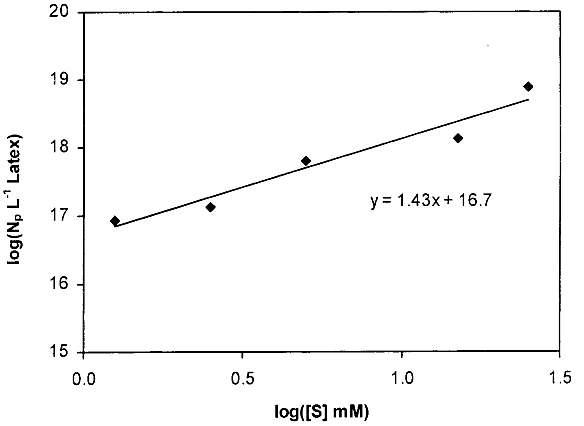

Figure 3. Dependence of the final number of particles on the surfactant concentration in TTOPS controlled miniemulsion polymerizations of styrene.

increase in the particle number with conversion. For the 1.25 and 2.5 mM surfactant concentrations, the particle number only increased slightly with increasing conversion. The surface tension of the miniemulsion prepared using 2.5 mM Dowfax 8390 was measured and found to be about 70 dyn/cm, which is close the value of deionized water and far above the surface tension of the Dowfax 8390 solution at its cmc (~50 dyn/cm). Therefore, not only do no micelles exist in this miniemulsion system, but also the surfactant coverage on the droplets is also relatively low. The slight increase in the number of particles during the polymerizations using 1.25 and 2.5 mM surfactant is attributed to some homogeneous nucleation of particles. Increasing surfactant concentration will increase the free surfactant concentration in the water phase and increase the probability of nucleating new particles during the polymerization. When the surfactant concentration was increased from 1.25 to 15 mM, the final volume-average particle size decreased from ~150 to ~60 nm. The particle number increased more than 10 times from 0.9×10^{17} to 14×10^{17} (number per liter latex). The dependence of the number of particles on the surfactant concentration is shown in Figure 3. It can be seen from the plot that the particle number is proportional to the 1.43 power of the surfactant concentration. Compared to the Smith−Ewart prediction of the particle number dependence on surfactant concentration ($N_p \propto [S]^{0.6}$), this result shows that particle number increased more with increasing surfactant concentration in the current nitroxide-mediated miniemulsion polymerization system stabilized by Dowfax 8390.

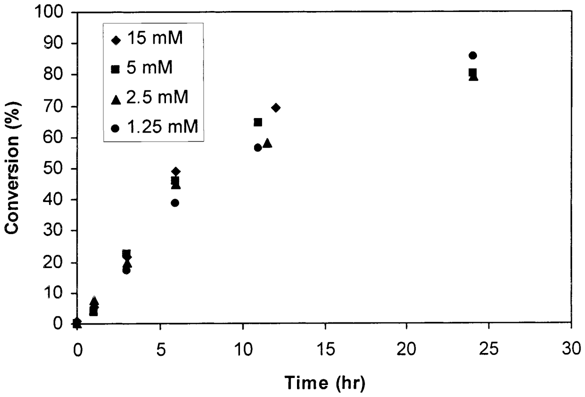

Figure 4. Conversion−time behavior of living free radical miniemulsion polymerizations of styrene with different surfactant concentrations; 3 wt % hexadecane on monomer; 2.5 wt % TTOPS-1500; T_r = 125 °C.

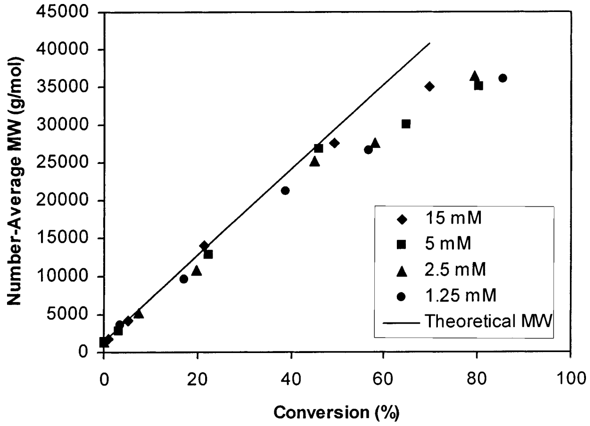

Figure 5. Evolution of the number-average molecular weight with conversion for living free radical miniemulsion polymerizations of styrene using different surfactant concentrations; 3 wt % hexadecane based on monomer and 2.5 wt % TTOPS-1500; T_r = 125 °C.

Despite the preceding similarities (increased particle number with increasing surfactant concentration), the nitroxide-mediated living free radical miniemulsion polymerizations show very different results in terms of the polymerization rate and molecular weight behaviors for the different surfactant concentrations compared to those reported for free radical miniemulsion polymerization systems. Figure 4 shows the conversion−time behavior of the living free radical polymerizations carried out with the different surfactant concentrations. The results indicate that when the surfactant concentration was increased from 1.25 to 15 mM, although the number of particles produced increased an order of magnitude, little effect on the polymerization rate was observed. A similar phenomenon is found with respect to the molecular weight. Figure 5 shows the evolution of the number-average molecular weight of the polymer obtained from the living free radical miniemulsion polymerizations with conversion for the different surfactant concentrations. In all cases, at lower conversions (<50%), the molecular weights agree well with the theoretical molecular weight calculated by assuming ideal chain extension. Deviations become significant when conversions exceed about 50%. Figure 6 shows the evolution of the molecular weight polydispersity index

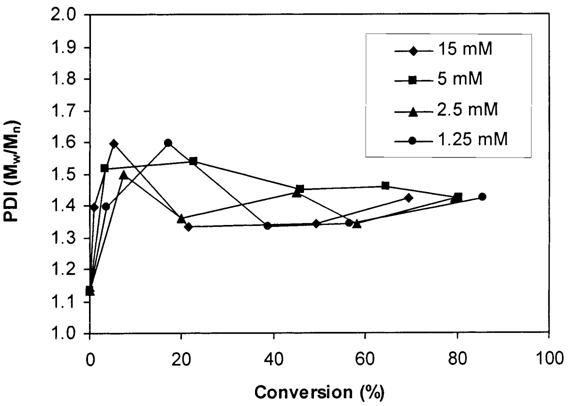

Figure 6. Evolution of the molecular weight polydispersity index with conversion for living free radical miniemulsion polymerizations of styrene using different surfactant concentrations; 3 wt % hexadecane based on monomer and 2.5 wt % TTOPS-1500; T_r = 125 °C.

(PDI = M_w/M_n) of the polymer obtained from the living free radical miniemulsion polymerizations with conversion. In all cases, the PDI increased from 1.14, the PDI of TTOPS, to 1.5−1.6 in the early stages of the polymerizations and decreased with conversion to a level between 1.3 and 1.5 as reported in previous work.[21] The PDI has no obvious dependence on the surfactant concentration. All these results show that there is no obvious effect of the surfactant concentration on the polymerization rate, molecular weight, and molecular weight distribution. These results indicate that the kinetics of living free radical miniemulsion polymerization differ significantly from those of a conventional miniemulsion polymerization.

The living free radical miniemulsion polymerization rate or molecular weight is not controlled by the number of particles. The significant kinetic differences between the living free radical miniemulsion polymerization and the conventional miniemulsion polymerization are mechanistic in nature. The key to the stable free radical controlled polymerization is the reversible termination reaction that occurs between the active free radical and the stable free radical:

$$P^* + N^* \underset{k_d}{\overset{k_c}{\rightleftharpoons}} P{-}N \tag{2}$$

where P* is the active free radical, N* is the stable free radical, and P−N is the dormant species which is the polymer chain capped by TEMPO. The equilibrium constant, K, is given by

$$K = k_d/k_c = [P^*][N^*]/[P{-}N] \tag{3}$$

The value of K has been measured in bulk polymerization to be 2×10^{-11} mol/L.[3] The concentration of dormant species, [P−N], is the concentration of TTOPS that is added as initiator. This concentration is approximately equal to the number of polymer chains if the amount of dead polymer chains in the system is negligible. [P−N] is at a level of 10^{-2} mol/L in the current system. [P*] was calculated from the kinetic data to be at a level of 10^{-8} mol/L at low conversion.[18] The stable free radical (TEMPO) concentration ([N*]) can be calculated from the equilibrium equation (2×10^{-5} mol/L). Assuming a 100 nm particle diameter, the average number of active species per particle ($\bar{n}$) can be estimated to be about 0.003. In the normal free radical emulsion polymerization of styrene, $\bar{n}$ is usually close to 0.5. This low number of active radicals per particle ($\bar{n}$ = 0.003) indicates that there is only one active propagating polymer chain among more than 300 particles in the system at any point in time, while all the other particles are dormant without active radicals. Besides $\bar{n}$, the average number of stable free radicals and the number of polymer chains per particle can also be calculated and used to explain the kinetic differences.

The average number of stable free radicals (i.e., TEMPO) is found to be about 6 per particle; that is, in each particle, with or without an active free radical, there are about this many stable TEMPO free radicals on average. Hence, whenever an active free radical appears in a particle, either from the dissociation reaction of dormant chains, or thermal initiation of styrene monomer, or by entry from the water phase, it will be deactivated by this excess number of stable free TEMPO radicals in a very short period of time.

The average number of polymer chains per particle is around 3000 in this estimation. Although the free TEMPO radical plays an important role in the kinetics of this reaction, it is still a low amount compared to the large number of polymer chains.

In a normal free radical emulsion or miniemulsion polymerization, the average number of free radicals per particle determines the average rate of polymerization per polymerization locus. Together with the number of particles in the system, $\bar{n}$, reflects the overall polymerization rate. In addition, the number of free radicals in a particle determines the activation or deactivation of the particle if another entry event occurs or a radical is generated in this particle. In conventional emulsion polymerization, for Smith−Ewart case 2 kinetics ($\bar{n}$ = 0.5), about half of the particles contain one radical each while the other half have none. From the approximate calculation above, it was found that the number of stable TEMPO free radicals per particle is high ($\bar{n}_{(\mathrm{stable})}$ = 6). Although these radicals will not contribute directly to the polymerization rate, they will effectively deactivate any active free radical(s) in a particle. So there are two kinds of $\bar{n}$ values in a living free radical polymerization system: (1) the average number of active free radicals per particle, referred to as $\bar{n}$, which is very low ($\bar{n}$ < 0.005), is used to evaluate the polymerization rate of the system; (2) the average number of total free radicals (including stable free radicals, which can deactivate the active free radical and stop the polymerization in the particle) per particle, referred to as $\bar{n}_{\mathrm{total}}$, is estimated to be around 6. This value can be used to evaluate the deactivation process of active free radicals.

In normal free radical miniemulsion polymerizations, propagation starts with the entry of a radical into a particle without a radical and stops when another radical enters or when a monomeric radical produced by chain transfer to monomer exits the particle. For a constant initiator concentration, temperature, and other conditions, the polymerization rate is controlled by the number of polymerization loci, the polymer particles. In the nitroxide-mediated miniemulsion system, when a radical enters or is generated in a particle, because there are several stable radicals in the particle, it will be deactivated within a very short period of time. Thus, the compartmentalization effect of radicals in these emulsion polymerization systems is overwhelmed by the controlling effect of stable free radicals present in the system. As a result, the polymerization rate shows little relationship to the number of particles and thus the surfactant concentration.

Conclusions

The effects of different surfactant concentrations on the particle size, particle number, polymerization rate, and molecular weight were studied in the living free radical miniemulsion polymerization system initiated with TTOPS. With increasing surfactant concentration, the particle size decreased and the particle number increased as expected. The particle number significantly increased with increasing conversion for the higher surfactant concentrations and was almost constant for the lower concentrations (1.25 or 2.5 mM Dowfax 8390). However, different surfactant concentrations had little effect on the molecular weight and the polymerization rate even though the number of particles increased more than 10 times going from the lowest to the highest concentration.

In a typical nitroxide-mediated living free radical miniemulsion polymerization system, at a stationary state, calculations show approximately one active free radical among more than 300 particles ($\bar{n}$ is about 0.003), 6 TEMPO free radicals per particle, and 3000 dormant polymer chains per particle. Because the coupling reaction between the TEMPO radicals and the active radicals overwhelms the compartmentalization effect of radicals in the miniemulsion polymerization, the surfactant concentration has little or no effect on the polymerization rate and molecular weight.

Acknowledgment. Financial support from the National Science Foundation under Grant CTS-9980208 is greatly appreciated.

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MA0206016