Nitroxide-Mediated Styrene Miniemulsion Polymerization

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Received January 2, 2001; Revised Manuscript Received October 3, 2001

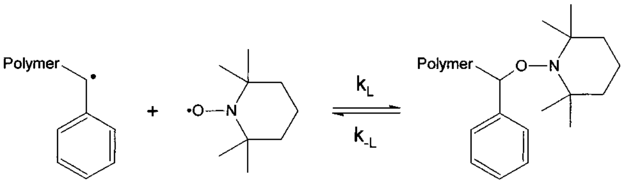
ABSTRACT: Living radical polymerization of styrene was conducted in a miniemulsion using TEMPO and the water-soluble initiator potassium persulfate (KPS). The effects of initiator concentration and the TEMPO:KPS ratio on conversion, molecular weight distribution, and particle size were studied. The miniemulsion polymerizations exhibit similar characteristics to bulk living radical systems but with unique features attributable to the heterogeneous nature of the system. There is a strong interaction between the KPS concentration and the TEMPO:KPS ratio, and therefore the effects of changing either variable depend strongly on the value of the other variable. Initiator efficiencies are considerably higher than in conventional KPS-initiated styrene emulsion or miniemulsion polymerizations, while the average number of active radicals per particle ($\sim 10^{-2}$) is much lower. Aqueous-phase kinetics and nitroxide partitioning determine the number of chains initiated and therefore also affect the polymerization rate and molecular weight.

Introduction

During the past several years, a variety of "living radical polymerization" or "controlled radical polymerization" systems have been reported. Examples of the various types include stable free radical polymerization (SFRP),[1] atom transfer radical polymerization (ATRP),[2] and reversible addition fragmentation chain transfer polymerization (RAFT).[3] These systems differ from conventional free radical systems in that most of the polymer chains continue to grow throughout the polymerization. In conventional radical polymerizations, chains may terminate by one of several mechanisms including bimolecular radical termination and transfer to monomer or other species, typically giving mean chain lifetimes of ∼0.1−1 s. In living radical polymerization, irreversible bimolecular termination reactions are significantly suppressed, although the chains are reversibly terminated. Living radical polymerizations do experience some irreversible termination reactions, albeit at a low rate, and therefore are not truly "living". However, they exhibit many of the features of living systems and offer improved control of the molecular weight distribution and the ability to synthesize polymers with tailored and/or complex microstructure.

The use of nitroxides in radical polymerizations was first reported by Rizzardo and Moad[4−7] and then later further developed by Georges and co-workers.[8−13] In nitroxide-mediated polymerizations, a nitroxide stable free radical is added to reversibly terminate the growing polymer chains. An equilibrium exists between inactive chains associated with a nitroxide and active chains (Scheme 1). The equilibrium is strongly shifted toward the inactive (dormant) species (e.g., for TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) at 125 °C, $K = 2.1 \times 10^{-11}$ mol L^{-1}),[14] so that capping of the active radical is sufficiently fast to compete with bimolecular termination. Consequently, the frequency of irreversible termination is much lower than in conventional free radical polymerizations, and hence relatively few chains terminate over the course of the reaction.

Scheme 1. Reversible Termination of Polystyrene Radical by TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy)



It has been shown that the reaction rate is quite sensitive to the concentration of "free" or "excess" nitroxide,[15] as would be expected from Scheme 1. High levels of free nitroxide result in a low concentration of active growing chains, which can reduce the polymerization rate to the point of complete inhibition. Consequently, reaction rates in nitroxide-mediated polymerizations are often lower than rates observed in conventional radical polymerizations. With monomers capable of thermal initiation (e.g., styrene), the thermally generated radicals act to reduce the free nitroxide concentration.[16,17] Monomers that do not easily autopolymerize (e.g., acrylates and methacrylates) are more difficult to polymerize with nitroxides, because the existence of even limited biradical termination causes a gradual increase in the free nitroxide concentration until the polymerization is completely suppressed. Acrylates/methacrylates may also be difficult to polymerize because of an unfavorable equilibrium between active and dormant chains. Addition of a slowly decomposing initiator can act as a source of radicals and has been shown to increase polymerization rates while maintaining a well-controlled polymerization.[18,19] Recently, several new nitroxide-based alkoxyamines have been shown to be effective for a variety of monomers, including 1,3-dienes, acrylates, acrylamides, and acrylonitrile.[20,21]

While nitroxide-mediated polymerizations in bulk have been well studied, comparatively little effort has

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10.1021/ma010006o CCC: $22.00

been directed toward heterogeneous reactions. Conducting a nitroxide-mediated polymerization in emulsion or miniemulsion could provide process advantages and would be an attractive route for commercial production of living radical polymers. Miniemulsion is similar to emulsion polymerization, but in miniemulsion the monomer droplets are small (∼0.05−0.2 μm) compared to the monomer droplets in emulsion (∼5−50 μm) and are the primary loci of nucleation. A costabilizer such as a long chain alkane is required to achieve the small monomer droplet size in miniemulsion.

Bon et al.[22] reported the first attempt to conduct a nitroxide-mediated polymerization in emulsion. Using seeded styrene emulsion polymerization initiated by the alkoxyamine 1-*tert*-butoxy-2-phenyl-2-(1-oxy-2,2,6,6-tetramethylpiperidinyl)ethane, they were able to achieve >99% conversion in 36 h. However, as conversion progressed, their molecular weight distributions displayed broadening to lower molecular weights. Marestin et al.[23] reported the first ab initio nitroxide-mediated styrene emulsion polymerization but experienced considerable difficulty in finding conditions that yielded a stable latex and reasonable conversions. They tried several different nitroxides but found many gave a coagulated latex and/or very low molecular weight and conversion.

Prodpran et al.[24,25] and Macleod et al.[26] were the first to report nitroxide-mediated styrene polymerization in miniemulsion. Prodpran et al., using benzoyl peroxide (BPO) and TEMPO, were able to produce stable latexes with over 90% conversion in 12 h. Molecular weights reached $M_n \sim 40$K, while polydispersities ranged from ∼1.15 to 1.60. However, they noted the difficulty of producing a colloidally stable latex in this temperature range. MacLeod et al. used the initiator KPS and TEMPO in their studies. The polydispersities they reported were consistently in the range 1.1−1.2.

Lansalot et al.[27] conducted batch emulsion and miniemulsion styrene polymerizations at temperatures below 100 °C using the nitroxide SG1 (*N*-*tert*-butyl-*N*-1-diethylphosphono-2,2-dimethylpropyl). Experiments were run using the oil-soluble initiator azobis(isobutyronitrile) (AIBN) and with an aqueous redox initiating system ($K_2S_2O_8$/$Na_2S_2O_5$). Runs using the oil-soluble initiator azobis(isobutyronitrile) (AIBN) gave fair polydispersities (1.6) but reached a limiting conversion of ∼60%. When an aqueous redox initiating system ($K_2S_2O_8$/$Na_2S_2O_5$) was used, the polymerization rates were greater but the polydispersity was >2, suggesting nonliving behavior. Farcet et al.[28] also conducted styrene miniemulsion polymerizations using SG1 with the aqueous redox system $Na_2S_2O_5$/$K_2S_2O_8$. They studied several factors, including initiator concentration, pH, and the monomer/water ratio. Most experiments showed relatively high polydispersities (>1.5) that were attributed to nitroxide partitioning into the aqueous phase, thereby leaving a low nitroxide concentration in the particles.

Ma et al.[29] studied nitroxide partitioning in styrene−water systems. They reported partition coefficients for TEMPO, 4-amino-TEMPO, and 4-hydroxy-TEMPO (4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy) in styrene−water mixtures at temperatures ranging from 25 to 135 °C. At 120 °C, the partition coefficient K for TEMPO is 110 ([mol/L TEMPO in styrene]/[mol/L TEMPO in water]), indicating that most of the TEMPO resides in the styrene phase. However, even small quantities of nitroxide in the aqueous phase may have a profound effect on the polymerization by affecting the aqueous-phase kinetics and reducing the free nitroxide level in the styrene phase.

We have conducted TEMPO-mediated polymerizations of styrene in miniemulsion using a water-soluble initiator. Miniemulsion was selected instead of emulsion because there is no significant particle nucleation in miniemulsion as there is in emulsion, thereby simplifying data interpretation. Instead, monomer droplets are directly nucleated to form particles. However, the chain initiation step will still occur in the aqueous phase since a water-soluble initiator is used. We have focused on the role of initiator concentration and the TEMPO:KPS ratio in determining conversion, molecular weight distribution, and particle size. Our interest in this work was in the differences between heterogeneous and homogeneous systems. The issues of chain initiation (especially in the presence of an aqueous phase initiator), particle size, and the evolution of molecular weight at the early stages of reaction were of primary concern.

Experimental Section

Styrene miniemulsion polymerizations were conducted under a nitrogen pressure of 240 kPa in a 300 mL stainless steel autoclave reactor, using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as the nitroxide. Potassium persulfate (KPS) was used as initiator, sodium dodecyl benzenesulfonate (SDBS) as surfactant, and hexadecane (HD) as costabilizer.

Materials. Styrene, TEMPO, SDBS, and HD were obtained from Sigma-Aldrich Canada Ltd. KPS was obtained from Fisher Scientific Ltd. All reagents were used as received unless otherwise specified.

Styrene was washed with a 2 wt % solution of NaOH in water to remove the inhibitor and then washed with distilled water three times. Water was removed by drying the styrene over calcium chloride overnight. The dried styrene was then distilled under high vacuum and refrigerated prior to use.

Miniemulsion Polymerization. SDBS was dissolved in deionized water to make up the aqueous phase. Hexadecane and TEMPO were dissolved in styrene to form the organic phase. These two solutions were mixed together with a stirring rod and homogenized to form a miniemulsion using a Microfluidizer-110S (Microfluidics International Corp.). The Microfluidizer was operated at 40 psi inlet pressure.

After the miniemulsion was loaded into the reactor, the initiator (KPS) was added. The reactor was sealed and the system purged with nitrogen six times to remove oxygen. The reactor was then pressurized with nitrogen to 240 kPa and heated to 135 °C. All polymerizations were run for 6 h. The heating stage took approximately 20 min.

Samples were withdrawn periodically from the reactor during polymerization and analyzed for fractional conversion, particle size distribution, and molecular weight distribution. Conversion was determined gravimetrically. Molecular weight distributions were obtained using a Waters 2690 separations module equipped with a Waters 410 differential refractometer and Waters Styragel columns. Data analysis was performed using Millennium 2010 software. A calibration curve was constructed from monodisperse polystyrene standards ranging in molecular weight from 8.7×10^2 to 2.8×10^6 amu. The eluant was tetrahydrofuran flowing at 1.0 mL/min and at a temperature of 30 °C. Capillary hydrodynamic fractionation (Matec Applied Sciences CHDF 2000) was used to determine particle size. The standard C-202 fractionation cartridge was used (particle diameter range from 15 to 1100 nm).

Results and Discussion

Obtaining a stable minemulsion is an important aspect of studying the kinetics of living radical polymerization. As noted by Prodpran et al.,[24] attaining

Table 1. Summary of Experimental Conditions and Results[a]

experiment	[KPS] (mM)	TEMPO (mmol)	HD (g)	Tempo:KPS	x	M_n	PDI	D_v (nm)
SFRMP-1	3.08	0.74	3.40	1.7	0.50	21 690	1.24	202
SFRMP-2	3.08	0.74	5.40	1.7	0.46	22 500	1.22	216
SFRMP-3	3.08	1.47	3.40	4.0	0.40	14 680	1.24	154
SFRMP-4	3.08	1.47	5.40	4.0	0.33	11 330	1.18	212
SFRMP-5	9.25	2.21	3.40	1.7	0.53	12 110	1.19	105
SFRMP-6	9.25	2.21	5.40	1.7	0.46	11 690	1.23	96
SFRMP-7	9.25	4.41	3.40	4.0	0.15	2410	1.11	293
SFRMP-8	9.25	4.41	5.40	4.0	0.16	2490	1.17	144
SFRMP-9[b]	6.16	2.21	4.37	2.9	0.38	12 920	1.15	183
SFRMP-10[b]	6.16	2.21	4.37	2.9	0.38	12 960	1.18	159
SFRMP-11[b]	6.16	2.21	4.37	2.9	0.39	12 320	1.18	155
SFRMP-12[c]	6.16	2.21	4.37	2.9	0.49	13 200	1.24	
SFRMP-13[c]	6.16	2.21	4.37	2.9	0.49	13 760	1.25	
SFRMP-14[c]	6.16	2.21	4.37	2.9	0.47	14 060	1.25	

[a] All experiments were run for 6 h at 135 °C using 30 g of distilled styrene, 0.88 g of SDBS, and 120 g of deionized water (PDI = M_w/M_n; D_v = volume average diameter). [b] Replicate runs at centerpoint condition using undistilled styrene. [c] Replicate runs at centerpoint condition using distilled styrene.

colloidal stability at higher temperatures represents a significant challenge. After experimenting with various surfactants, the suitability of using SDBS as a surfactant and HD as costabilizer was established. While SDBS may undergo some decomposition at 135 °C and was found to be unsuitable for nitroxide-mediated conventional emulsion polymerization,[23] it did prove to be an effective surfactant in our system. For all the experimental conditions, reactor fouling and coagulum were minimal.

Experiments were run at nine different experimental conditions. Eight of these conditions (SFRMP-1 through SFRMP-8) were designed to study the effects of initiator concentration, TEMPO:KPS ratio, and HD concentration. The factors were varied independently, each at two levels, to ensure the observed effects due to each variable were uncorrelated with the other variable. The remaining runs are two sets of three replicates, done at the beginning of the study to establish the reproducibility of the experimental results. The conditions used in the replicate runs (concentrations of KPS, TEMPO, and HD) were at the "centerpoint" of the other conditions (i.e., at the midrange value of the other experiments). Runs SFRMP-9 to SFRMP-11 were run with unpurified styrene while runs SFRMP-12 to SFRMP-14 were run with distilled styrene. As shown in Table 1, reproducible and well-controlled polymerizations are obtained even using unpurified styrene; however, the conversions at 6 h are lower than when distilled styrene is used. (This corresponds to a longer induction period observed for the runs using unpurified styrene.) Figure 1 shows excellent reproducibility in the conversion−time data of runs SFRMP-12 to SFRMP-14. The final molecular weights are comparable for the two sets of replicates despite the conversion differences, indicating the number of chains is higher when the styrene is distilled. For runs SFRMP-1 through SFRMP-8, distilled styrene was used.

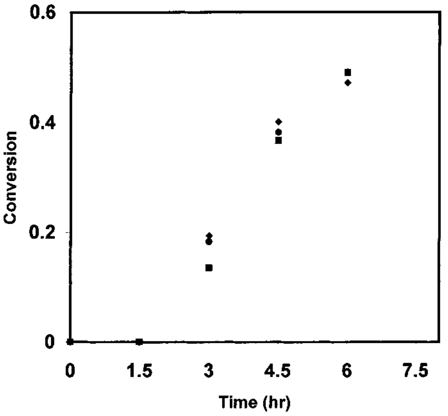

Figure 1. Reproducibility of conversion−time plots for centerpoint runs (SFRMP-12, SFRMP-13, SFRMP-14).

Table 2. Stability of Mean Monomer Droplet Sizes under Nonpolymerizing Conditions (135 °C)[a]

time (h)	D_v (nm)	$(D_{84}/D_{50})^{0.5}$	time (h)	D_v (nm)	$(D_{84}/D_{50})^{0.5}$
0	151	1.33	4	190	1.61
1	173	1.42	5	186	1.59
2	179	1.52	6	188	1.60
3	182	1.55			

[a] D_v = volume average diameter; $(D_{84}/D_{50})^{0.5}$ = geometric standard deviation. Measurements made using Malvern Mastersizer 2000.

Little is known about the colloidal stability of styrene/water miniemulsions at temperatures over 100 °C, yet this issue is important in understanding the process behavior. To determine the stability of an unpolymerized miniemulsion, the monomer droplet size distribution was monitored over a 6 h period at 135 °C using a Malvern Mastersizer 2000. Excess *tert*-butylcatechol (1500 ppm) was added to the styrene to prevent thermal polymerization. As seen in Table 2, the volume mean droplet size was relatively stable during this period. There was an increase in D_v from 150 to190 nm, while the geometric standard deviation increased from 1.3 to 1.6, signifying a slight broadening of the distribution. No noticeable change in the droplet size distribution is observed upon heating. It is possible that the hexadecane concentration in the droplets at 135 °C is slightly higher than at 25 °C; however, this effect should be quite small since the HD solubility in water is still slight.

Farcet et al.[28] showed that pH can be an important variable for living radical miniemulsions polymerizations mediated by the nitroxide SG1. SG1 degrades readily at low pH in the absence of styrene. In our experiments, KPS decomposition results in the pH of the solution dropping to ∼2.5−3 for all conditions by the time the reactor reaches 135 °C. There is no change in the pH for the remainder of the run. It is possible that the stability of TEMPO is also pH-sensitive, and there may be some TEMPO degradation due to the acidic conditions although we did not investigate the effect of pH.

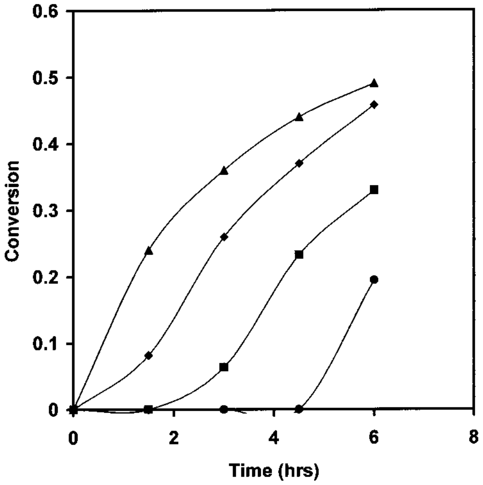

Figure 2. Conversion vs time behavior for all runs: SFRMP-2 (◆) [KPS] = 3.08 mM, TEMPO:KPS = 1.7: SFRMP-4 (■) [KPS] = 3.08 mM, TEMPO:KPS = 4.0: SFRMP-6 (▲) [KPS] = 9.25 mM, TEMPO:KPS = 1.7: SFRMP-8 (●) [KPS] = 9.25 mM, TEMPO:KPS = 4.0.

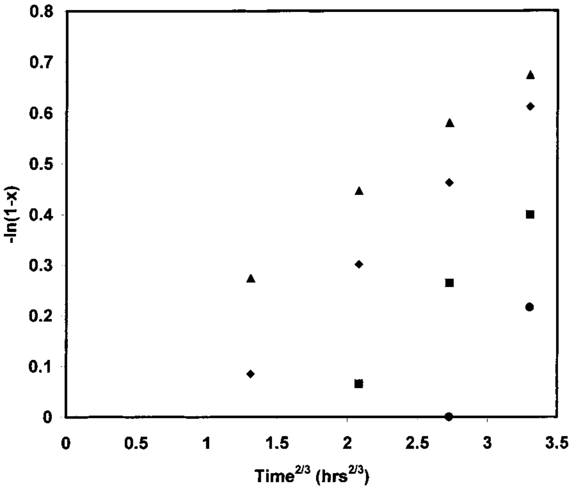

Figure 3. Relationship between $-\ln(1 - x)$ and time$^{2/3}$: SFRMP-2 (◆) [KPS] = 3.08 mM, TEMPO:KPS = 1.7: SFRMP-4 (■) [KPS] = 3.08 mM, TEMPO:KPS = 4.0: SFRMP-6 (▲) [KPS] = 9.25 mM, TEMPO:KPS = 1.7: SFRMP-8 (●) [KPS] = 9.25 mM, TEMPO:KPS = 4.0.

Effect of Hexadecane (HD) Level. Two different HD concentrations were used for the designed experiments. Experiments SFRMP-1,3,5,7 were run with 3.4 g of HD, while SFRMP-2,4,6,8 were run with 5.4 g of HD. With the exception of SFRMP-7 and SFRMP-8, increasing the HD level resulted in slightly lower conversion. In SFRMP-7 and SFRMP-8, the conversions at 6 h were relatively low due to prolonged induction periods, and therefore differences may not be as apparent. There were no noticeable changes in colloidal stability upon changing the HD level. At the higher HD level, monomer concentration is lower in the particles. In addition to a direct dilution effect, this also means the rate of thermal initiation is lower at the higher HD levels. It has been shown in nitroxide-mediated styrene polymerizations that the rate is largely determined by the thermal polymerization rate,[14] and therefore use of a higher HD level can be expected to reduce conversions. The trends and behaviors observed for the effects of KPS concentration and the TEMPO:KPS ratio were very similar for either HD level, and therefore for the remainder of this paper, only the runs with high HD concentration (SFRMP-2,4,6,8) runs will be discussed.

Effect of KPS Concentration and TEMPO:KPS Ratio on Conversion. Two TEMPO:KPS ratios (1.7:1 and 4.0:1) were used, each at two KPS concentrations (Table 1). The lower TEMPO:KPS ratio corresponds to slightly fewer nitroxide molecules than primary radicals arising from KPS decomposition while the higher ratio corresponds to two TEMPO molecules for each primary radical arising from KPS decomposition. A possible concern in these systems is the reaction of KPS with TEMPO, but it has been shown that in the presence of monomer this reaction is unlikely to be significant.[30]

Figure 2 shows conversion vs time for runs SFRMP-2,4,6,8. Induction periods were often seen in our experiments, particularly at higher TEMPO:KPS ratios, and are caused by initially high concentrations of free nitroxide. As the free nitroxide level drops due to thermally generated radicals and side reactions that may consume TEMPO, the equilibrium shifts more in favor of active radicals and polymerization commences. The effects of [KPS] on conversion can be seen by comparing SFRMP-2 to SFRMP-6 (TEMPO:KPS = 1.7) and by comparing SFRMP-4 to SFRMP-8 (TEMPO:KPS = 4.0). At the low TEMPO:KPS ratio, increasing the [KPS] by a factor of 3 (3.08−9.25 mM) results in only a small increase in the final conversion at 6 h, although larger differences are observed at lower times.

When the TEMPO:KPS ratio is 4.0, the effects of varying [KPS] are different. First is should be noted that a lengthy induction period is seen at both KPS concentrations at the higher TEMPO:KPS ratio. Paradoxically, increasing [KPS] 3-fold at this TEMPO:KPS ratio results in a longer induction period and a lower final conversion.

The effects of varying the TEMPO:KPS ratio on conversion at different KPS concentrations are seen by comparing SFRMP-2 to SFRMP-4 ([KPS] = 3.08 mM) and SFRMP-6 to SFRMP-8 ([KPS] = 9.25 mM) in Figure 2. At the low [KPS], increasing the TEMPO:KPS ratio from 1.7 to 4.0 results in a longer induction period, but the profiles of the two curves are very similar in appearance. However, when [KPS] = 9.25 mM, increasing the TEMPO:KPS ratio leads to more dramatic differences between the two curves. The induction period becomes considerably longer at the high TEMPO:KPS ratio (>4.5 h), resulting in a much greater difference in final conversions than is seen when [KPS] = 3.08 mM.

Figure 3 shows $-\ln(1 - x)$ plotted against time$^{2/3}$ for all runs. Fischer[31] determined this plot should be linear for ideal living systems. The plots are approximately linear with varying intercepts signifying different induction periods. Some downward curvature may be present toward the end of the run, which could arise from dead chains produced by disproportionation of the growing chains or bimolecular termination.

Figures 2 and 3 collectively reveal the presence of a pronounced interaction effect between the amount of initiator used and the ratio of TEMPO:KPS employed. When interpreting and generalizing experimental results for these systems, it is not sufficient to consider only one of either the KPS concentration or the TEMPO:KPS ratio in isolation from the other. The quantitative and qualitative effect of changing either variable depends strongly on the value chosen for the other variable. As will be discussed in subsequent sections,

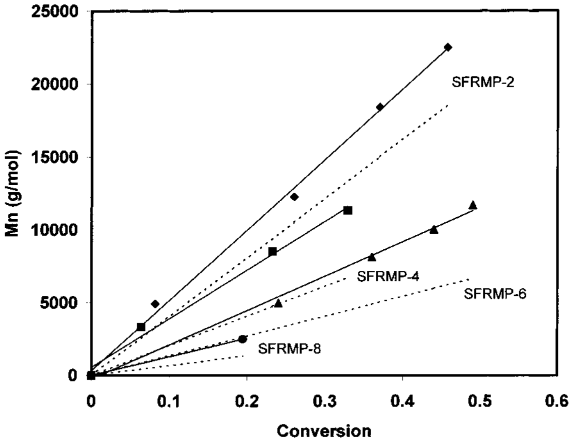

Figure 4. Evolution of number-average molecular weight with conversion. Dotted lines are theoretical molecular weights based on amount of TEMPO used. SFRMP-2 (◆) [KPS] = 3.08 mM, TEMPO:KPS = 1.7: SFRMP-4 (■) [KPS] = 3.08 mM, TEMPO:KPS = 4.0: SFRMP-6 (▲) [KPS] = 9.25 mM, TEMPO: KPS = 1.7: SFRMP-8 (●) [KPS] = 9.25 mM, TEMPO:KPS = 4.0.

the nature of the interaction effect is related to the initiator efficiency, which is primarily determined by the aqueous-phase reactions occurring in the initial phase of the polymerization.

At a TEMPO:KPS ratio of 1.7, increasing the amount of initiator increases the conversion slightly whereas at a TEMPO:KPS ratio of 4.0, increasing the amount of initiator actually decreases the conversion. This seemingly anomalous result can be attributed to higher free nitroxide concentrations in the particles that lead to rate suppression. Higher free nitroxide levels imply there are fewer living chains per mole of TEMPO, suggesting that initiator efficiency decreases with increasing initiator concentration, reflecting the role of aqueous-phase kinetics and chain nucleation. These issues are further explored later.

Molecular Weights. The evolution of the number-average molecular weight is an important indicator of the "livingness" of the system. In a living system, M_n is linearly proportional to conversion. Downward curvature in a plot of M_n vs conversion indicates an increase in the number of chains, which for styrene polymerizations occurs through thermal initiation. For all experiments in our study, M_n varied linearly with conversion (Figure 4). The slopes of the curves decrease with increasing TEMPO concentration, although the KPS concentration also plays a role in determining the number of chains. At both low and high TEMPO:KPS ratios, increasing the KPS concentration resulted in lowering of molecular weight, indicating an increase in the number of chains, although as will be shown later, the decrease in molecular weight is not directly proportional to the increase in [KPS]. The theoretical M_n values (based on the amount of TEMPO) are also shown in Figure 4. In most cases the experimental M_n is notably higher than theoretical M_n. The discrepancy is attributable to two factors. First is the nonstoichiometric ratio of TEMPO to KPS, and second is the limited initiator efficiency. Runs with a TEMPO:KPS ratio of 4.0 (SFRMP-4,8) have a large initial excess TEMPO concentration and therefore low theoretical M_n. Runs SFRMP-2,6, with a near-stoichiometric TEMPO:KPS ratio of 1.7, would be expected to exhibit experimental M_n close to theoretical values, but their limited initiator efficiency results in fewer chains being nucleated and thus higher experimental molecular weights.

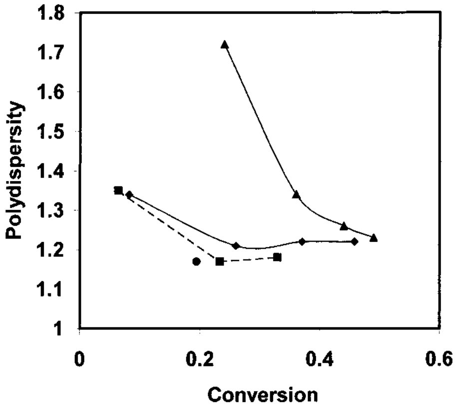

Figure 5. Evolution of polydispersity with conversion: SFRMP-2 (◆) [KPS] = 3.08 mM, TEMPO:KPS = 1.7: SFRMP-4 (■) [KPS] = 3.08 mM, TEMPO:KPS = 4.0: SFRMP-6 (▲) [KPS] = 9.25 mM, TEMPO:KPS = 1.7: SFRMP-8 (●) [KPS] = 9.25 mM, TEMPO:KPS = 4.0.

The final polydispersity (PDI) for all runs was in the range 1.08−1.24. Figure 5 shows the relationship between PDI and conversion. As is seen in nitroxide-mediated bulk systems, the PDI decreases with conversion. The PDI values shown in Figure 5 are similar to those observed in bulk systems. SFRMP-6 stands out in that the initial polydispersity was significantly higher than the other runs.

Initiator Efficiencies. The number of polymer chains generated provides a wealth of information and is critical in determining the molecular weight and the reaction rate. Two of the more instructive ways to present this information are to calculate (1) the ratio of polymer chains to TEMPO and (2) the ratio of the number of chains to the number of primary radicals potentially arising from initiator decomposition. Figure 6a shows the ratio of the number of chains/TEMPO as a function of conversion for the different experiments. (The number of chains was calculated as the moles of styrene polymerized divided by number-average chain length.) The two experiments at low [KPS] (SFRMP-2 and SFRMP-4) show an increase in the number of chains/TEMPO during the run, while SFRMP-6 (high [KPS]) shows a slight decrease. An increase in the number of chains would result from thermally generated radicals, while biradical termination decreases the total number of chains. The runs with higher TEMPO:KPS (SFRMP-4 and SFRMP-8) display low values, consistent with the large excess of TEMPO initially present in these runs. When the low TEMPO:KPS ratio is used (SFRMP-2, SFRMP-6), the number of chains/TEMPO is higher and even approaches one for SFRMP-2. Similar trends were observed by Prodpran et al.,[25] who reported a continuous increase in the number of chains with conversion at TEMPO:BPO ratios of 1.25 and 1.35 but a constant number of chains at a ratio of 3.00.

It is instructive to compare "apparent" initiator efficiencies (defined as the number of polymer chains divided by the number of initiator derived radicals, assuming all the KPS decomposes to yield two radicals per KPS molecule). Figure 6b shows that the ratio of the number of chains/(2[KPS]) varies with conversion and ranges from ~0.6 to 1.2. Increasing the TEMPO: KPS ratio at a given [KPS] increases the number of chains/(2[KPS]). A TEMPO:KPS ratio of 4.0 gave initia-

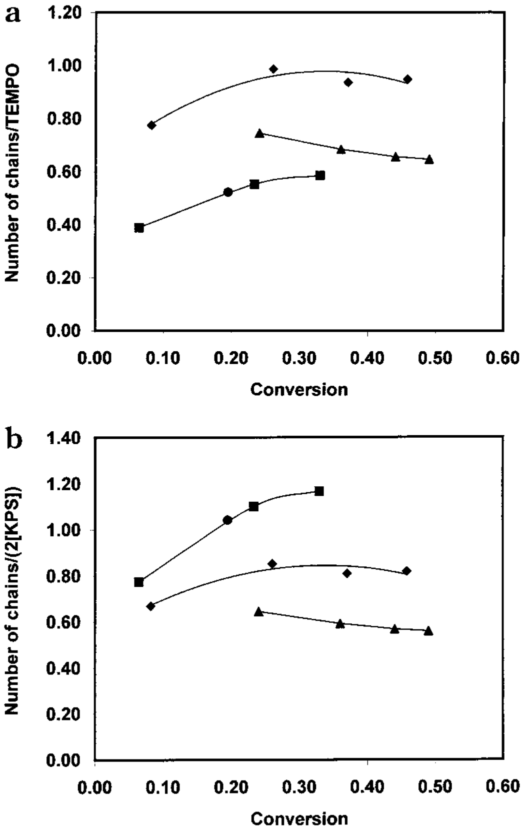

Figure 6. (a) Variation in number of chains/TEMPO with conversion: SFRMP-2 (◆) [KPS] = 3.08 mM, TEMPO:KPS = 1.7: SFRMP-4 (■) [KPS] = 3.08 mM, TEMPO:KPS = 4.0: SFRMP-6 (▲) [KPS] = 9.25 mM, TEMPO:KPS = 1.7: SFRMP-8 (●) [KPS] = 9.25 mM, TEMPO:KPS = 4.0. (b) Variation in number of chains/(2[KPS]) with conversion. Legend as above.

tor efficiencies ~1, signifying nearly all of the KPS-derived radicals initiated chains. In contrast, at TEMPO:KPS = 1.7, efficiencies are lower. Furthermore, increasing the [KPS] results in a decrease in efficiency. A drop in efficiency with initiator concentration at a given TEMPO:KPS ratio directly impacts the free nitroxide concentration by effectively increasing the moles of nitroxide available per mole of living chains, thus suppressing the rate as was observed experimentally.

Initiator efficiencies in classical styrene emulsion polymerization are usually <10% for this range of initiator concentrations.[32] The comparatively high efficiencies observed in our system suggest that reversible deactivation of aqueous oligomeric radicals by nitroxide reduces the loss of aqueous radicals by bimolecular termination and thus increases the overall initiator efficiency. At higher initiator concentrations, aqueous biradical termination rates are higher, leading to fewer chains being initiated.

Particle Size Distributions. The final particle size distributions of the miniemulsion latexes are broad, with mean volume average particle diameters (D_v) varying from about 100 to 200 nm (Table 3). Broad particle size distributions are characteristic of many miniemulsion polymerization systems and may indicate a prolonged particle nucleation period. The possibility of significant homogeneous nucleation cannot be ignored in this system, particularly since at 135 °C the styrene solubility is considerably higher than that at the typical temperature range for emulsion polymerizations.[29] Extensive homogeneous nucleation could result in a pronounced increase in surfactant demand that may impact the overall colloidal stability. Coalescence of particles and/or monomer droplets must also be considered, especially at these elevated temperatures where attaining colloidal stability is known to be more difficult, although the stability of our droplet size measurements suggests this may not be a serious concern.

Table 3. Particle Size Averages for Miniemulsion Polymerizations[a]

experiment	D_v (nm)	D_n (nm)	D_w/D_n
SFRMP-2	216	179	1.69
SFRMP-4	212	189	1.35
SFRMP-6	96	79	1.84
SFRMP-8	144	83	3.48

[a] Samples measured after 6 h. D_v = volume average diameter; D_n = number-average diameter; D_w/D_n = polydispersity factor.

Table 4. Number of Chains Per Particle and Average Number of Active Radicals per Particle ($\bar{n}$) for Final Samples

experiment	[KPS], mM	TEMPO:KPS (molar)	no. of chains/particle	$\bar{n}$
SFRMP-2	3.08	1.7	48 200	3.67×10^{-2}
SFRMP-4	3.08	4.0	64 800	3.10×10^{-2}
SFRMP-6	9.25	1.7	8680	1.96×10^{-3}
SFRMP-8	9.25	4.0	54 700	1.37×10^{-2}

As previously shown (Table 2), the mean monomer droplet diameter (D_v) at the beginning of polymerization is approximately 150 nm. SFRMP-2 and SFRMP-4, which use a low concentration of KPS, both show final D_v values over 200 nm, implying inefficient droplet nucleation. (The relatively good stability of the unpolymerized droplets (Table 2) suggests coalescence is not a major concern.) Both runs with the higher KPS concentration showed smaller final particle diameters. (SFRMP-6: D_v = 96 nm, D_n = 79 nm; SFRMP-8: D_v = 144 nm, D_n = 83 nm). SFRMP-8 showed nearly the same final diameter (D_v) as the initial droplets, while SFRMP-6 was considerably smaller, implying homogeneous nucleation played an important role at this condition. Both runs had small D_n values, suggesting the presence of small particles and the possible occurrence of homogeneous nucleation for both runs. A high KPS concentration coupled with the lower TEMPO:KPS ratio of 1.7 for SFRMP-6 would result in a large excess of primary radicals upon KPS decomposition, possibly leading to increased growth rate of aqueous oligomers and subsequent homogeneous nucleation. At a TEMPO:KPS ratio of 4.0 (SFRMP-8), more primary radicals survive to initiate chains (Figure 6), but the large excess of TEMPO results in a greater probability of those aqueous radicals being reversibly deactivated prior to propagating to the chain length required for homogeneous nucleation.

Average Number of Radicals per Particle. While in a conventional styrene emulsion polymerization there will usually be no more than one growing chain in a particle, in an emulsion-based nitroxide-mediated system that value is considerably higher, although most of those chains will be inactive. Table 4 shows the calculated total number of chains per particle in our experiments after 6 h. Values were calculated using conversion, M_n, and particle size data. The number of chains per particle is on the order of 10^4. However, most of these chains are dormant at any given time, and therefore it is more useful to calculate $\bar{n}$, which gives a measure of the number of active radicals per particle. Table 4 also shows $\bar{n}$ for the final samples ($\bar{n}$ was

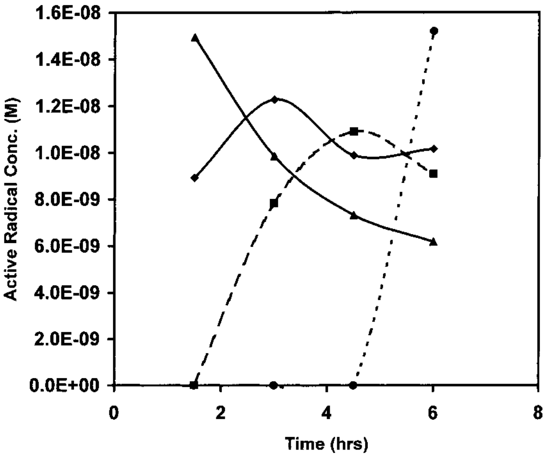

Figure 7. Evolution of the active radical concentration with time: SFRMP-2 (◆) [KPS] = 3.08 mM, TEMPO:KPS = 1.7: SFRMP-4 (■) [KPS] = 3.08 mM, TEMPO:KPS = 4.0: SFRMP-6 (▲) [KPS] = 9.25 mM, TEMPO:KPS = 1.7: SFRMP-8 (●) [KPS] = 9.25 mM, TEMPO:KPS = 4.0.

calculated using $R_p = k_p[M]_p\bar{n}N_p/N_A$, where $k_p = 2936$ dm^3 mol^{-1} s^{-1},[33] $[M]_p$ is the monomer concentration in the particles, N_p is the number of particles per liter of aqueous phase, and N_A is Avogradro's number). The rate at each time was approximated from the slope of the conversion–time plot at that time. (A smoothed line was drawn through the data, and the tangent to the smoothed line was used as the slope.) The final two data points were used to estimate the slope at the final sampling time. Typical $\bar{n}$ values are ~10^{-2}, well below those in conventional emulsion or miniemulsion polymerization (~0.5). These low values of $\bar{n}$ are consistent with the low polymerization rates observed in our experiments. SFRMP-6 shows lower values of both $\bar{n}$ and number of chains/particle than the other runs, which is primarily a reflection of its much smaller particle size (high particle number).

For comparative purposes, the active radical concentration was also calculated for each run as a function of time, assuming that bulk kinetics were obeyed (Figure 7). Active radical concentrations $[R^\bullet]$ were calculated using $R_p = k_p[M]_p[R^\bullet]$. The calculated values of $[R^\bullet]$ are all ~10^{-8} M, which is approximately typical of bulk SFRP systems. For all runs, the active radical concentration is expected to increase from zero to some maximum value and thereafter slowly decrease due to nitroxide accumulation arising from bimolecular termination.[31] Figure 7 reveals that the active radical concentration decreases steadily for SFRMP-6 during the times for which data are available, while for SFRMP-2 the concentration is approximately constant. When excess nitroxide is initially present (e.g., SFRMP-4,8), a long period of time may be required before the increase in $[R^\bullet]$ is observed. With an initial deficiency of nitroxide (e.g., SFRMP-2,6), the maximum value in $[R^\bullet]$ will occur at very early times, and only the decrease in $[R^\bullet]$ may be observed experimentally.

Compartmentalization in Heterogeneous Nitroxide-Mediated Polymerizations. Conventional free radical polymerizations exhibit inherently different kinetics in emulsion as compared to bulk due to compartmentalization effects, in which the loci of polymerization (i.e., the polymer particles) become sufficiently small that the overall kinetic behavior is affected. Although the chains are indeed segregated in our miniemulsion system, the kinetics of chain activation/deactivation will not result in rate enhancement as observed in conventional emulsion polymerization. However, as particle size decreases, the likelihood of two macroradicals being activated at the same time may decrease to an extent where radical–radical termination occurs less frequently than in larger particles. Consequently, the accumulation of TEMPO due to termination would be slowed in the smaller particles, and the resulting rate could also be higher. Butté et al.[34] discussed the issue of compartmentalization effects in various types of emulsion-based living radical systems. They predicted that for SFRP and ATRP the kinetics of the chain activation/deactivation steps should result in $\bar{n}$ values (and thus rates) much lower than seen in conventional styrene emulsion polymerization and that compartmentalization effects (higher rates and molecular weights) would not be evident. However, Charleux came to somewhat different conclusions in a theoretical treatment of controlled radical polymerization in dispersed systems.[35] In simulations of styrene polymerizations at 90 °C mediated by the nitroxide SG1, Charleux calculated that broader polydispersities (especially at low conversions) and higher conversions will become apparent for particles with diameters in the 50–100 nm range. Although the polydispersity increases, the fraction of chains that are living is higher due to a decreased irreversible termination rate. As noted by Charleux, these calculations cannot be directly applied to higher temperature polymerizations where thermal polymerization is important. However, the effect of increasing thermal polymerization is to decrease the active radical concentration, which will increase the particle diameter at which compartmentalization effects become evident.

Experiment SFRMP-6 displays anomalous behavior in two aspects. (SFRMP-6 had the high KPS concentration (9.25 mM) and a TEMPO:KPS ratio of 1.7.) The PDI of SFRMP-6 is initially very high (1.72) before decreasing to a final value of 1.23. In contrast, the initial PDI of the other runs is ~1.3. In addition, the conversion of SFRMP-6 is unusually high when compared to SFRMP-2. Given the higher initiator efficiency of SFRMP-2, and the fact that both experiments have the same TEMPO:KPS ratio, SFRMP-6 should have a higher initial ratio of free nitroxide to polymer chains. Lower conversions are therefore expected for SFRMP-6 compared to SFRMP-2, although the observed conversions are in fact higher.

One possible cause is a period of insufficient nitroxide early in the run.[25] At a TEMPO:KPS ratio of 1.7, there are fewer TEMPO molecules than potential primary radicals arising from KPS decomposition. Approximately 2% of the TEMPO will be partitioned into the aqueous phase under our conditions, slightly increasing any potential deficiency of nitroxide in the particles. The expected result of a nitroxide deficiency is a poorly controlled reaction, with faster monomer consumption and a broad molecular weight distribution. While the observed conversions and the initial polydispersity of SFRMP-6 are high, the final polydispersity is low, indicating the polymerization is well-controlled. Furthermore, expected behavior is seen for both conversion and molecular weight (Figures 3 and 4), implying this explanation is not correct.

A more plausible explanation is related to the small particle size of SFRMP-6. The particle diameter for SFRMP-6 is significantly smaller than in the other runs, which may be related to more particles being initially nucleated under these conditions. Smaller particle size can lead to compartmentalization of the kinetics. It is therefore plausible that SFRMP-6, which has a significantly smaller particle size than the other runs, is displaying signs of compartmentalization in its kinetic behavior as evidenced by high initial polydispersity and higher than expected conversions. The pronounced decrease in the calculated active radical concentration for SFRMP-6 (Figure 7) is also consistent with a compartmentalization argument. New particles produced by homogeneous nucleation would initially be very small, and therefore compartmentalization effects would be strong. However, as those particles grew with conversion, the effects of compartmentalization would be less apparent, leading to lower rates of polymerization.

Conclusions

TEMPO-mediated living radical polymerizations were run in miniemulsion using KPS as initiator. Colloidal stability of the miniemulsion was excellent, with essentially no coagulum formation or reactor fouling under any of the experimental conditions. The monomer droplets were found to be relatively stable at 135 °C under nonpolymerizing conditions. Plots of $-\ln(1 - x)$ vs time$^{2/3}$ were linear with some evidence of curvature at higher conversions, likely due to termination. Nonzero intercepts in the plots of $-\ln(1 - x)$ vs time$^{2/3}$ were generally observed, indicating the presence of induction periods. Length of the induction period depends on the initial excess nitroxide concentration, which is determined by both the TEMPO:KPS ratio and the initiator efficiency. There is a strong interaction between the KPS concentration and the TEMPO:KPS ratio, so that the qualitative and quantitative effects of changing either variable vary considerably depending on the value of the other variable. Initiator efficiencies were much higher than typically observed in conventional emulsion or miniemulsion polymerization, reflecting the role of aqueous TEMPO in deactivating aqueous-phase radicals. At a ratio of TEMPO:KPS = 4.0, efficiencies were ~100%. The average number of active radicals per particle is $\sim 10^{-2}$, much lower than conventional emulsion or miniemulsion polymerization. Although compartmentalization effects on rate or molecular weight distribution are generally not expected to appear for most miniemulsion systems with larger particle size, such effects may appear with small particles. The probable presence of homogeneous nucleation under conditions of high initiator concentration and low TEMPO:KPS yielded a smaller particle diameter, with high initial polydispersities and conversions consistent with compartmentalization effects.

Acknowledgment. Financial support of the Natural Sciences and Engineering Research Council of Canada, Materials and Manufacturing Ontario, and the Xerox Research Centre of Canada is gratefully acknowledged.

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MA010006O