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Nitroxide-Mediated Living Free Radical Miniemulsion Polymerization of Styrene

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ABSTRACT: The miniemulsion technique was applied to the controlled/living free radical polymerization of styrene utilizing TEMPO-terminated oligomers of polystyrene (TTOPS) as a macroinitiator species to initiate the polymerization at 125 °C. Miniemulsion polymerizations of styrene using different amounts of TTOPS were studied. It was found that the polymerization rate of a miniemulsion containing no TTOPS was significantly faster than those containing TTOPS. In the latter reactions, the molecular weight of the polymer increased almost linearly with conversion up to 75% conversion. The slope of the molecular weight vs conversion curve increased with decreasing TTOPS concentration as expected. Particle size distributions were measured by both TEM and CHDF and were found to be broad. Using the kinetics and particle size data, the average number of active free radicals per particle ($\bar{n}$ in classical emulsion polymerization systems) was estimated and found to be low (≤ 0.005).

Introduction

Emulsion polymerization has developed into a widely used process for the production of synthetic polymeric materials. One of the most important characteristics of the emulsion polymerization process is the radical segregation within the polymerization loci, namely the polymer particles. The number of these polymerization sites is typically within a few orders of magnitude of the number of radicals generated. Therefore, emulsion polymerizations can simultaneously produce high polymerization rates and high polymer molecular weights. This is the key feature of emulsion polymerization that distinguishes it from other polymerizations such as bulk, solution, and suspension polymerization. Miniemulsions are relatively stable submicron (50−500 nm) spherical oil droplets suspended in an aqueous phase prepared by an emulsification process using a combination of an ionic surfactant and a costabilizer such as a long chain alkane or fatty alcohol.

Anionic polymerizations of vinyl monomer were the first living polymerization reported in 1956.[1] Living polymerizations are characterized by controlled molecular weights, desired end groups, and narrow molecular weight distributions. The ideal living polymerization reaction does not have any termination or transfer reactions. Until recently, living polymerization was limited to ionic polymerization. In radical polymerization, the bimolecular termination between two growing radicals is hard to avoid, and initiation is comparatively slow while propagation is fast. Hence, high molecular weight polymers are formed from the very beginning of the reaction, and consequently the molecular weight distributions become broadened. However, there are several approaches to control radical polymerization. Living/controlled free radical polymerizations are typically divided into three categories:[2] stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP), and reversible addition fragmentation chain transfer polymerization (RAFT). SFRP in bulk systems has been thoroughly studied.[3−12] However, comparatively little has been reported using this technique in emulsion polymerization[13,14] or dispersion polymerization.[15]

This article will focus on the application of the SFRP technique in miniemulsion polymerizations. The stable free radical used here is 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO). The key aspect of the polymerization in the presence of TEMPO that brings about the pseudoliving character of the polymerization is believed to be the reversible combination of an active propagating radical, P*, with the stable free radical, N*, which itself cannot initiate polymerization, to form a dormant species, P−N:

$$\mathrm{P^*} + \mathrm{N^*} \underset{k_\mathrm{d}}{\overset{k_\mathrm{c}}{\rightleftharpoons}} \mathrm{P{-}N} \tag{1}$$

$$K = k_\mathrm{d}/k_\mathrm{c} = [\mathrm{P^*}][\mathrm{N^*}]/[\mathrm{P{-}N}] \tag{2}$$

where k_c and k_d are the reaction rate coefficients for the combination and dissociation reactions, respectively. K is the equilibrium constant. [P*], [N*], and [P−N] are the molar concentrations of polymer free radicals, stable TEMPO radicals, and dormant species comprised of TEMPO-capped polymer chains, respectively.

Much work has been reported on bulk polymerizations using stable free radicals.[3−5] The free radical concentrations in a living free radical polymerization have been described by the following differential equations:[3]

$$\mathrm{d}[\mathrm{P^*}]/\mathrm{d}t = R_\mathrm{i} - k_\mathrm{t}[\mathrm{P^*}]^2 + k_\mathrm{d}[\mathrm{P{-}N}] - k_\mathrm{c}[\mathrm{P^*}][\mathrm{N^*}] \tag{3}$$

$$\mathrm{d}[\mathrm{N^*}]/\mathrm{d}t = k_\mathrm{d}[\mathrm{P{-}N}] - k_\mathrm{c}[\mathrm{P^*}][\mathrm{N^*}] \tag{4}$$

Here R_i is the rate of initiation due to initiator derived radicals and/or thermally generated radicals, and k_t is the radical termination rate constant between two active radicals (P*). When the temperature is raised and the system reaches steady state,

$$\mathrm{d}[\mathrm{P^*}]/\mathrm{d}t = \mathrm{d}[\mathrm{N^*}]/\mathrm{d}t = 0 \tag{5}$$

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so

$$[\mathrm{P^*}] = (R_\mathrm{i}/k_\mathrm{t})^{1/2} \quad (6)$$

and

$$[\mathrm{N^*}] = K[\mathrm{P{-}N}]/[\mathrm{P^*}] \quad (7)$$

Therefore, the polymerization rate is given by

$$R_\mathrm{p} = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_\mathrm{p}[\mathrm{P^*}][\mathrm{M}] = ({k_\mathrm{p}}^2 R_\mathrm{i}/k_\mathrm{t})^{1/2}[\mathrm{M}] \quad (8)$$

Thus, the polymerization rate in this system should be independent of the TEMPO−PS adduct concentration and dependent on the rate of the thermal production of radicals. Even the thermal polymerization rate (i.e., no added TEMPO−PS adduct) should be the same. Fukuda et al. obtained experimental results that were well described by the preceding kinetic scheme.[3]

The primary objective of this research is to study the kinetics and mechanism of stable free radical polymerization in a heterogeneous polymerization system producing submicron latex particles. Recently, a study on the miniemulsion polymerization of styrene initiated with TEMPO and benzoyl peroxide (BPO) was reported.[14] In this report, TEMPO-terminated oligomers of polystyrene (TTOPS) are used instead as the initiator. The primary reason for using TTOPS as initiator instead of TEMPO/BPO is to simplify the system. Since the initiation efficiency of benzoyl peroxide in this system is not easily determined, it is difficult to control the number of polymer chains initiated. By using TTOPS as the initiator, the initial number of chains can be specified, and the expected molecular weights of these are readily estimated assuming that the monomer adds to all of these chains and only these chains. 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.

In any kinetic study of emulsion polymerization, the average number of free radicals per particle, $\bar{n}$, is one important parameter used in understanding the nature of the reaction. In this paper, $\bar{n}$ or the average number of active propagating radicals per particle is estimated for living free radical miniemulsion polymerizations of styrene. The effect, if any, of compartmentalization in this reaction system will be evaluated.

Experimental Section

Styrene (Aldrich) monomer was cleaned before use by passing it over activated alumina to remove the inhibitor, while the remaining reagents were used as received. DOWFAX 8390 (disulfonated alkyl diphenyl oxide sodium salt; Dow Chemical Co.), an anionic surface active 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 in the presence of benzoyl peroxide (BPO) (0.09 mol/dm^3) and TEMPO (0.108 mol/dm^3). The reactants were preheated for 1 h at 90 °C followed by 7 h polymerization at 125 °C. Polymer was retrieved by precipitation in an excess of methanol and purified by three dissolution/precipitation cycles using toluene and methanol. The yield was 71%, and the number-average molecular weight measured by gel permeation chromatography (Waters Styragel columns HR3, HR4, HR6, Waters 410 differential refractometer detector) was 7050 g/mol (TTOPS-7050) with a polydispersity index ($M_\mathrm{w}/M_\mathrm{n}$) of 1.24.

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

ingredient	weight (g)	concentration
	Water Phase	
deionized water	65	
Dowfax-8390	1.04	25 mM[b]
	Oil Phase	
styrene	15.6	
hexadecane	1.47	100 mM[b]
TTOPS-7050	0.0−3.1	0−20 wt %[c]

[a] Total final solids ∼20% (based on 100% conversion). [b] Based on water phase, [hexadecane]/[Dowfax] = 4:1 mole ratio. [c] Based on styrene monomer.

The recipe for the miniemulsion polymerization is shown in Table 1. TTOPS-7050 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 at a power output setting of 8 and a duty cycle of 50% for 10 min. After purging the miniemulsion with nitrogen for 1 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 after first cooling the system to about 90 °C. 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 both transmission electron microscopy (TEM, Phillips 400) and capillary hydrodynamic fractionation (CHDF, MATEC Applied Sciences, model 1100).

Results and Discussion

Effect of the Presence of TTOPS on the Miniemulsion Polymerization Rate. Several publications have described the use of TEMPO-terminated oligomers as initiator in bulk polymerization.[3−5] Here, results using TTOPS macroinitiator in living miniemulsion polymerizations of styrene are reported. Two concentrations of TTOPS-7050, 5% and 20%, were used while keeping all other ingredients the same as given in Table 1. A control experiment is included for comparison where no TEMPO, TTOPS, or any other initiator was added. This polymerization was initiated with styrene radicals thermally generated by the Mayo mechanism,[17,18] and since no stable free radicals were present, this was not a living free radical polymerization (referred to as 0% TTOPS). Stable latexes were obtained in all cases. Figure 1 shows the conversion of styrene as a function of time for the various TTOPS concentrations. Obviously, the purely thermal miniemulsion polymerization of styrene (no TTOPS or TEMPO) was significantly faster than those containing TTOPS. The two polymerizations containing 5% and 20% TTOPS-7050 are similar to each other, though the polymerization containing 5% TTOPS-7050 is slightly faster than that containing 20% TTOPS-7050. More detailed kinetic data are needed to determine whether there is any significant effect of the TTOPS concentration on the miniemulsion polymerization rate. The polymerization rates shown here are similar to those reported for bulk polymerizations by Fukuda et al.[3] (similar conversions for 5 h polymerization). However, in contrast to the results shown here, the bulk polymerization rate of styrene without TTOPS was the same as with 10% TTOPS (referred to as PS−TEMPO adducts) in the first 3 h, up to 30% conversion. Equation 6 indicates that

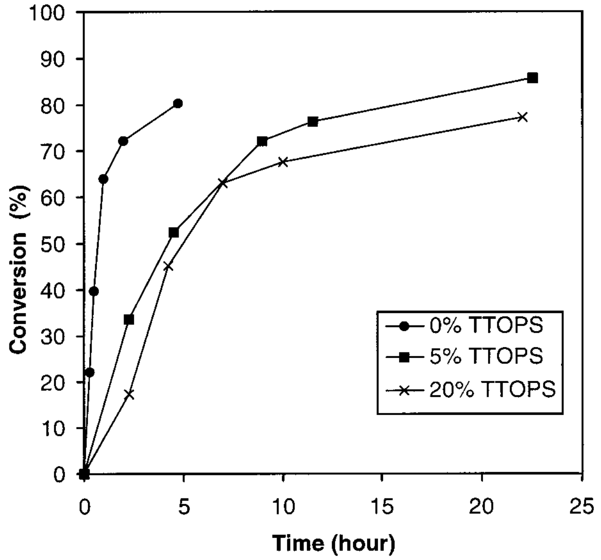

Figure 1. Conversion vs time behavior of styrene miniemulsion polymerizations with and without TTOPS. TTOPS concentrations were 0% (control), 5%, and 20%; $T_r = 125$ °C.

the polymerization rate of a living free radical polymerization should be the same as a normal free radical polymerization. In the miniemulsion thermal polymerization (no TTOPS), the polymerization rate is obviously faster. The reason for the faster polymerization rate in the miniemulsion system is the high level of radical segregation. Radicals in different particles cannot terminate with each other. However, the segregation effect is not significant with the presence of TEMPO. TEMPO radicals can rapidly and reversibly react with active free radicals in each droplet or particle. The TEMPO radicals regulate the average number of active free radicals per particle to a low level. The effects of radical segregation on the termination rate becomes insignificant compared to the effect of the presence of TEMPO in the living free radical miniemulsion polymerization. The average number of active free radical per particles will be calculated and discussed further.

Evolution of Molecular Weights and Polydispersities. An important aspect of living polymerization is the linear increase in the molecular weight with conversion. In these stable free radical controlled miniemulsion polymerizations, the number-average molecular weights (M_n) were also observed to increase linearly up to 75% conversion. Figure 2a shows the evolution of M_n for the polymers obtained from the miniemulsion polymerizations initiated with the two TTOPS-7050 concentrations. Figure 2b shows the evolution of M_n for the polymer obtained from miniemulsion polymerization without TTOPS. Since the latter is not a living polymerization, the molecular weight evolution obtained is totally different from the other two; high molecular weight (about 330 000 g/mol) polymer was formed from the beginning of the polymerization and with a broad distribution (PDI = 2.5) and remained unchanged up to 70% conversion. M_n decreased thereafter with increasing polydispersity (see Table 2).

In the polymerizations initiated with TTOPS-7050, the amount of TTOPS determines the initial number of growing chains in the system. At a given conversion, the different numbers of polymer chains, as determined by the initial amount of added TTOPS, will share the same amount of styrene monomer that has reacted. Thus, the higher TTOPS concentration should result in a lower molecular weight. This is observed here. From the conversion and initial concentration of TTOPS, the theoretical molecular weight can be calculated on the basis of the assumption of a constant number of polymer chains and that every TTOPS chain participates in adding monomer. The measured and theoretical molecular weights for both cases are presented in Table 2 and shown in Figure 3. The theoretical molecular weights are always higher than the experimental values, and the difference increases with conversion. This difference could be caused by an increasing number of polymer chains in the system resulting from the thermal generation of new free radicals and/or a population of low molecular weight dead polymers resulting from termination reactions.

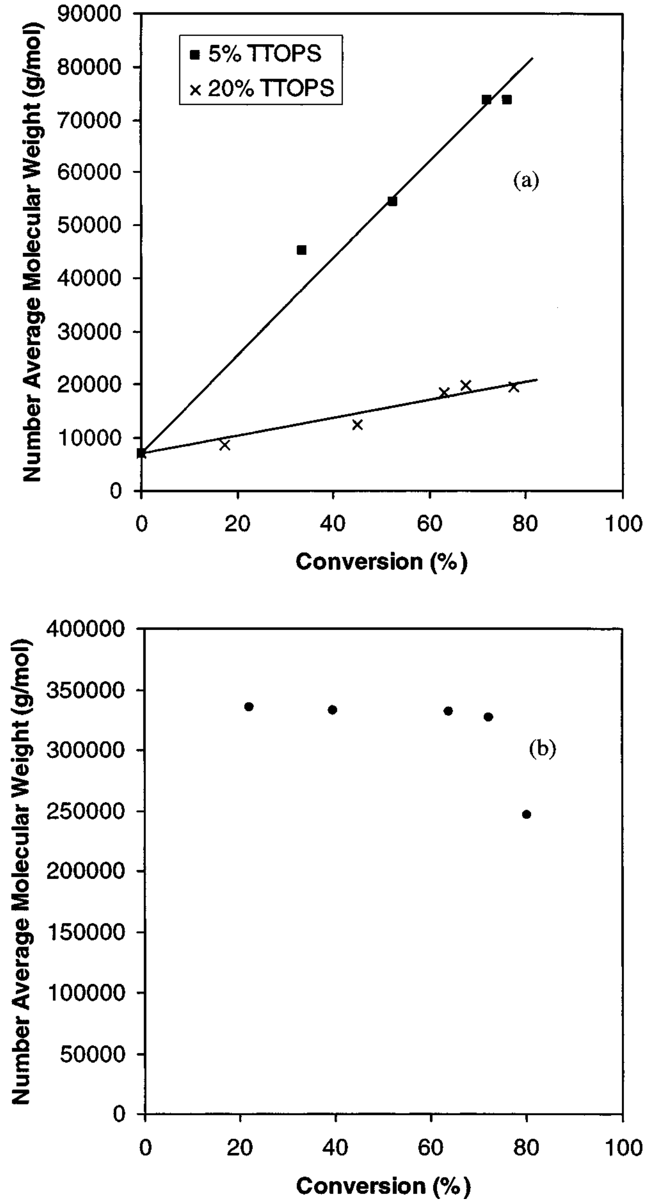

Figure 2. Number-average molecular weight as a function of conversion for (a) miniemulsion polymerizations of styrene carried out with 5% and 20% TTOPS-7050 and (b) without TTOPS or TEMPO (thermal polymerization); $T_r = 125$ °C.

The deviation from the ideal living polymerization also resulted in an increase in the molecular weight polydispersity index. As the conversion increased, the

Table 2. Experimental and Theoretical Molecular Weight as a Function of Conversion for the Miniemulsion Polymerizations Using 5% and 20% TTOPS-7050

sample	conv (%)	M_n (g/mol)	PDI	calcd M_n (g/mol)
		0% TTOPS-7050		
1	22.2	334 700	2.50	
2	39.6	332 000	2.52	
3	63.9	331 800	2.46	
4	72.2	327 000	2.51	
5	80.4	246 200	3.24	
		5% TTOPS-7050		
0	0.0	7 050	1.24	7 050
1	33.7	45 100	1.65	52 824
2	52.5	54 400	1.75	78 440
3	72.0	73 600	1.74	104 985
4	76.3	73 800	1.76	110 824
		20% TTOPS-7050		
0	0.0	7 050	1.24	7 050
1	17.3	8 730	1.24	13 289
2	45.1	12 400	1.40	23 277
3	63.1	18 400	1.54	29 765
4	67.5	19 800	1.73	31 355
5	77.4	19 700	1.86	34 917

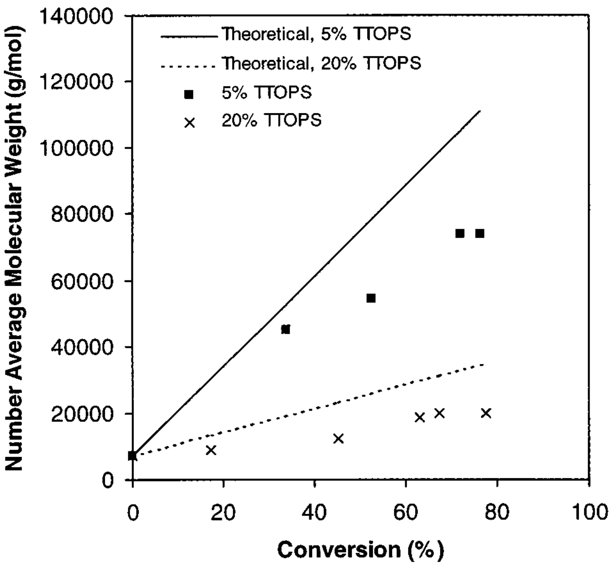

Figure 3. Experimental and theoretical number-average molecular weight as a function of conversion for miniemulsion polymerizations of styrene carried out with 5% and 20% TTOPS-7050; T_r = 125 °C.

molecular weight distributions became broader. In the case of 20% TTOPS-7050, the polydispersity index increased gradually from 1.24 (0% conversion, TTOPS-7050) to 1.54 (63% conversion). Then it increased more abruptly to 1.86 when the conversion reached 77.4%. Similar phenomena can also be observed in the case of 5% TTOPS. There are several reasons for the more significant divergence at high conversions: irreversible termination and thermal initiation of styrene monomer. Dead polymer chains form when irreversible termination occurs. Newly terminated polymer chains have a molecular weight similar to the living chains (by disproportional termination or combination with a monomer radical). However, as the conversion increases, the living chains continue to grow to higher molecular weights while the dead chains do not and are observed as deviations. The number of dead chains accumulates in the system with increasing conversion. Thermal initiation occurs at all times during the polymerization, generating new and shorter polymer chains still regulated by TEMPO. From the conversion–time curves (Figure 1), it can be seen that it takes less than 2 h for the conversion to exceed 15%, while it takes 10 h or more to increase only 10% beyond 70% conversion. At low conversions, newly generated polymer chains are closer in molecular weight to the existing living chains. Therefore, the deviations become more significant with increasing conversion.

The molecular weight distribution of the polymer produced using 20% TTOPS-7050 is narrower than that using 5% TTOPS-7050 up to 65% conversion. The results in Table 2 suggest that the polydispersity decreases with increasing TTOPS concentration. These changes in the polydispersity indicate how well the free radical polymerizations are controlled. Better control of the polymerization means having a reaction that is closer to the ideal living polymerization conditions, resulting in narrower molecular distributions and little or no increase in the polydispersity index with conversion. The polymerization rate, which is proportional to the active free radical concentration [P*], is not dependent on the concentration of dormant species, [P–N], as mentioned before. Equation 7 indicates that increasing [P–N] increases [N*] in the system. With a higher TEMPO radical concentration, the active free radicals (P*) are more likely to react with the TEMPO to form dormant species (P–N) rather than being irreversibly terminated by another active free radical to form dead polymer. Thus, the polymerization is better controlled.

Particle Size and Size Distribution of Latexes. Figure 4 shows TEM micrographs of latex particles obtained from the living free radical miniemulsion polymerizations using the two TTOPS-7050 concentrations: (a) 20% TTOPS-7050 and (b) 5% TTOPS-7050. These micrographs show broad particle size distributions. From the micrographs, it can be seen that although the majority of the particles have diameters around 60 nm, there are many off-size large particles with diameters well over 100 nm. Some particles have diameters even larger than 450 nm (not shown in Figure 4). These large particles are 100 or 1000 times larger in volume (or weight) than most other particles. Although the large particles are few in number, they are crucially important in the particle size weight distribution. The particle size distributions of the 5% TTOPS-7050 latex as measured from the TEM images are shown in Figure 5. A total of 4260 particles were measured on the micrographs for establishing these distributions. The number distribution curve (Figure 5a) has a single peak at about 60 nm with a tail of larger particles, while the weight distribution curve shows multiple peaks for particle sizes greater than 200 nm. These multiple peaks are not reproducible, however. This may indicate that the multiple-peak distribution does not represent the true distribution and may simply result from the limited sample size of the measurement even though 4260 particles were measured in this case. Among all the particles measured to produce the particle size distribution in Figure 5, there was only one particle with a diameter larger than 450 nm, and this can be seen in the weight distribution (Figure 5b). This peak resulting from just one particle can account for the poor reproducibility of the particle size weight distribution curve. The particle size distributions were also measured by capillary hydrodynamic fraction (CHDF), which also indicated multiple peaks and irreproducibility of the particle size weight distribution curve (Figure

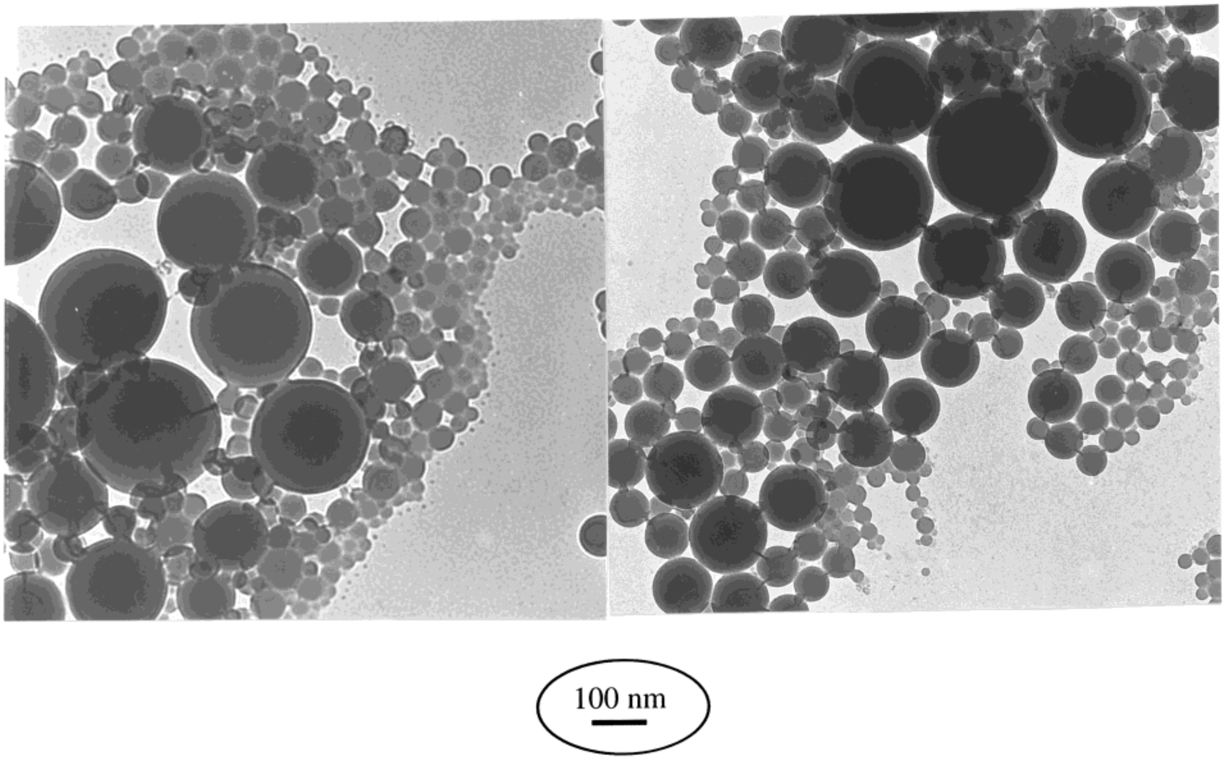

Figure 4. TEM images of the final latexes prepared by living free radical miniemulsion polymerization of styrene with different amounts of TTOPS-7050: (a, left) 5% TTOPS-7050 and (b, right) 20% TTOPS-7050.

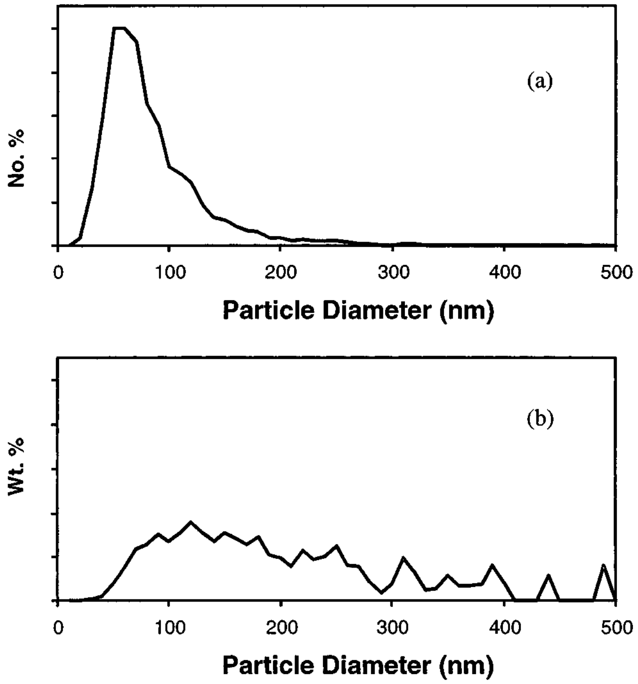

Figure 5. Particle size distributions of the final latex prepared by living free radical miniemulsion polymerization of styrene initiated with 5% TTOPS-7050 measured by TEM: (a) number distribution and (b) weight distribution (4260 particles were measured).

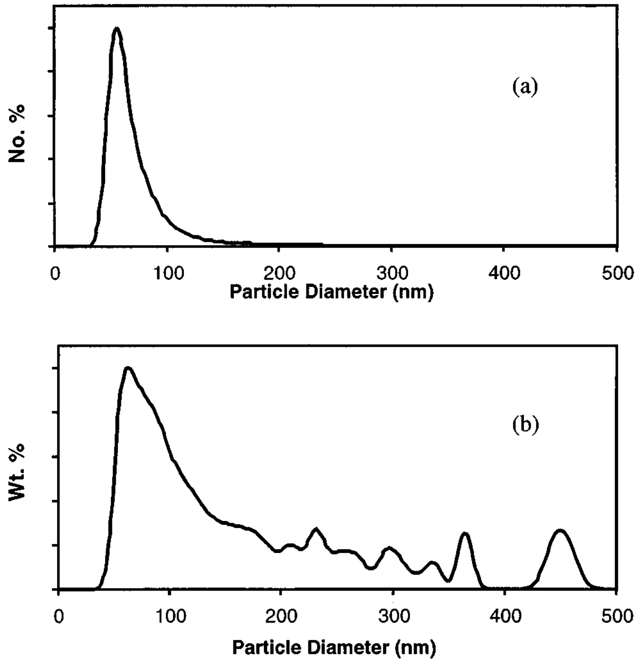

Figure 6. Particle size distributions of the final latex prepared by living free radical miniemulsion polymerization of styrene initiated with 5% TTOPS-7050 as measured by CHDF: (a) number distribution and (b) weight distribution.

6). This irreproducibility is hard to avoid in the case of such a broad distribution, unless many thousands or even tens of thousands of particles are counted in the measurements by either TEM or CHDF. However, when the irreproducibility of the weight distribution curve does not significantly affect the particle size averages, then the average value of particle size can be used. The volume-average particle sizes presented here and used in later calculations are those measured by CHDF. Figure 7 shows the evolution of the particle size and particle number with conversion for the latexes prepared by living free radical miniemulsion polymerizations initiated with 5% and 20% TTOPS. In addition, the control latex prepared by nonliving miniemulsion without TTOPS is also included. In all case, the number of particles increased up to about 70% conversion and

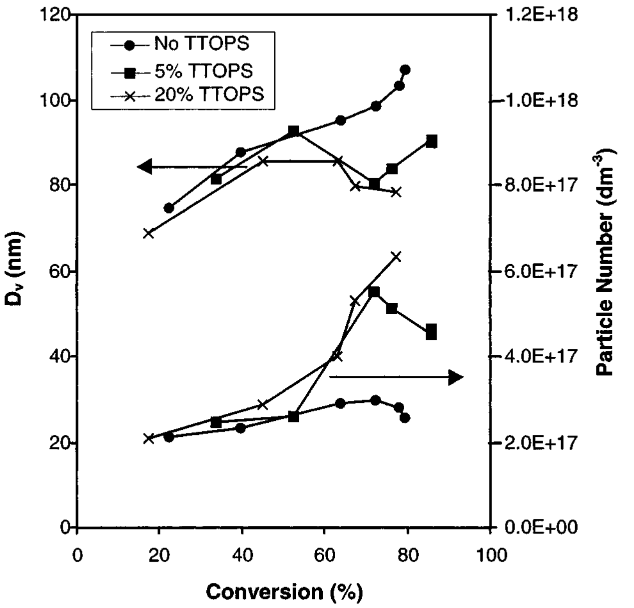

Figure 7. Evolution of particle size and particle number of latexes prepared by miniemulsion polymerization of styrene initiated with 0%, 5% and 20% TTOPS-7050 as measured by CHDF.

then decreased for 0% and 5% TTOPS. This decrease is an indication of some limited aggregation occurring in these systems. The mechanism of the nucleation of new particles has yet to be determined.

Kinetics of Living Free Radical Miniemulsion Polymerization (Calculation of $\bar{n}$). In an emulsion polymerization, the average number of free radicals per particle, $\bar{n}$, is typically calculated by knowing the monomer concentration in the particles, $[M]_p$ (based on the conversion), the rate of polymerization, R_p, and the number of particles, N_p:

$$\bar{n} = \frac{R_p N_A}{k_p[M]_p N_p} \tag{9}$$

where k_p is the propagation rate constant (dm^3/(mol s)) and N_A is Avogadro's number. This approach can be readily applied to these miniemulsion polymerizations.

Consider the miniemulsion polymerization employing 5% TTOPS-7050 and having a 20% final solids content. From the conversion−time curve (Figure 8a), the monomer concentration vs time profile was obtained (Figure 8b) by assuming that the monomer and polymer are present at the same concentrations in all the reaction loci (i.e., monomer droplets/polymer particles). The lines in the graphs represent a polynomial fit of the data. The polymerization rate, R_p, is defined as

$$R_p = -\,d[M]/dt \tag{10}$$

The polymerization rate vs time curve can therefore be obtained as presented in Figure 8c. Using eq 8, [P*] can be calculated ($[P^*] = R_p/(k_p[M])$). The value of k_p at 125 °C can be calculated according to the reported methods[16] to be 2300 dm^3 mol^{-1} s^{-1}. The evolution of [P*] with conversion is shown in Figure 8d. Up to 70% conversion, the active free radical concentration in the particles decreased gradually from 2.0×10^{-8} to 1.5×10^{-8} mol/dm^3. When the conversion exceeded 70%, the active free radical concentration decreased steeply, and the polymerization almost stopped at a conversion between 80% and 90% because of the extremely low active free radical concentration (1.4×10^{-9} mol/dm^3). There are two reasons for the accelerated decrease in

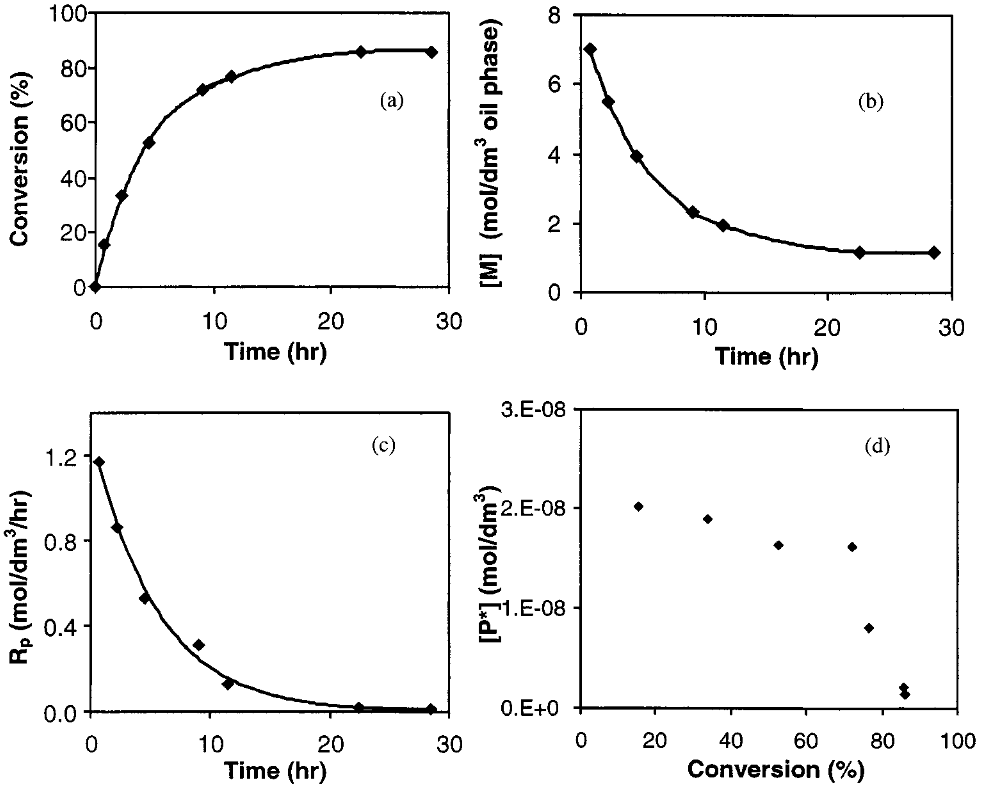

Figure 8. Kinetics of the living free radical miniemulsion polymerization of styrene with 5% TTOPS-7050, T_r = 125 °C: (a) conversion vs time; (b) monomer concentration vs time; (c) polymerization rate vs time; (d) active propagating free radical [P*] concentration vs conversion.

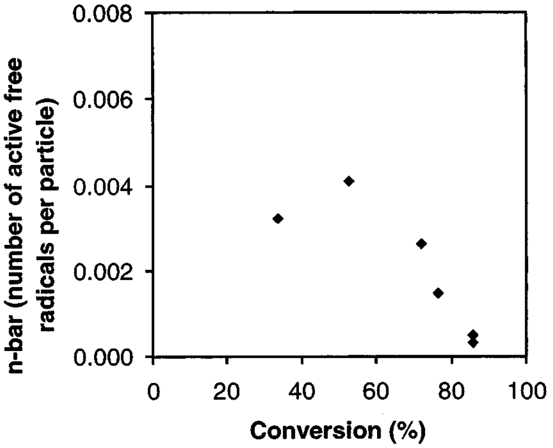

Figure 9. Evolution of $\bar{n}$ with conversion in the living free radical miniemulsion polymerization of styrene using 5% TTOPS-7050; $T_r = 125$ °C.

[P*] at high conversion. First, at steady state, [P*] is dependent on the initiation rate, R_i (eq 4), which strongly depends on the monomer concentration ($R_i \propto [M]^3$).[17] When the conversion is high, the supply of newly generated thermal free radicals becomes small, while the active free radicals continuously, though slowly, irreversibly terminate with each other, causing [P*] to decrease. Second, when irreversible termination occurs, free TEMPO radicals are formed, [N*] increases, and eq 1 shifts to the right side, resulting in lower [P*] values.

The volume average particle size (D_v) was obtained from CHDF measurements for the corresponding conversions at various times. The evolution of $\bar{n}$ with conversion is shown in Figure 9 for the polymerization employing 5% TTOPS-7050. $\bar{n}$ is seen to be in the range of (3−4) × 10^{-3} up to 60% conversion. Similarly low values of $\bar{n}$ were also estimated for the miniemulsion polymerization initiated with 20% TTOPS as shown in Figure 10a. $\bar{n}$ values for the thermally initiated miniemulsion polymerization (0% TTOPS) of styrene are almost 1 order of magnitude higher than those with TTOPS, although the values are still low (0.015−0.03). Obviously, the differences are due to the presence of TEMPO free radicals in the two former cases.

Smith−Ewart case 1 kinetics describes the situation where $\bar{n} \ll 0.5$. However, the reason for the low values in conventional emulsion polymerizations is quite different from that in living free radical miniemulsion polymerizations. In Smith−Ewart case 1, a low $\bar{n}$ is the result of a high rate of radical exit from the polymer particles relative to the radical entry rate. However, the monomer used in this work is styrene, which is a hydrophobic monomer. Furthermore, although some monomer radicals are generated thermally or by transfer, the majority of the active radicals are polymer radicals with more than 70 monomer units which have no possibility of exiting into the aqueous phase. Therefore, such low $\bar{n}$ values should not result from a comparably high exit rate of radicals from the particles. It is more likely that the low $\bar{n}$ values are caused by the slow free radical generation rate, resulting in low free radical concentrations. Furthermore, the TEMPO radicals present, which are excellent radical scavengers, will regulate the concentration of free radicals to an even lower concentration.

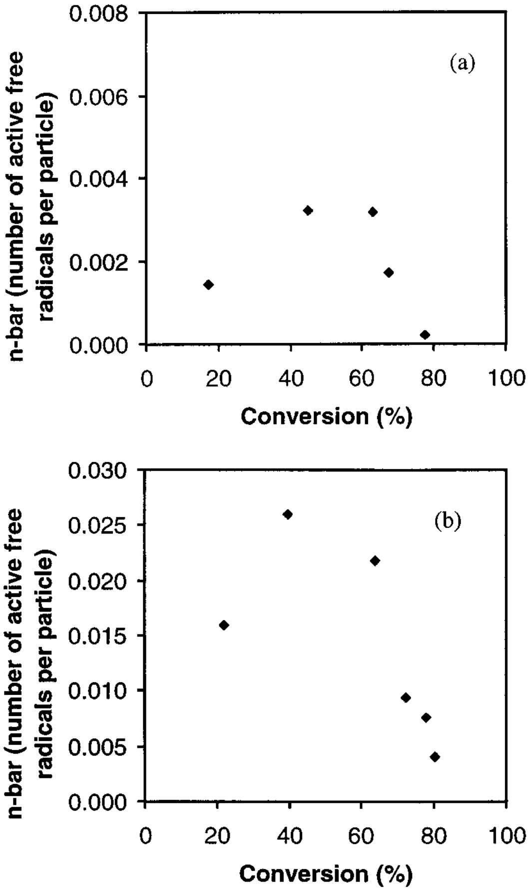

Figure 10. Evolution of $\bar{n}$ with conversion in the miniemulsion polymerization of styrene using (a) 20% TTOPS-7050 and (b) 0% TTOPS; $T_r = 125$ °C.

Since $\bar{n}$ is in the range 0.003−0.004, this means that only one in 250−330 particles contains an active free radical at any given time. This results in a low probability of having two active free radicals present in a single particle at the same time, which is necessary for an irreversible termination reaction. These low values of $\bar{n}$ thus imply a low termination rate in these polymerization systems.

Conclusions

Stable latexes were prepared at 20% solids by living/controlled free radical miniemulsion polymerization of styrene utilizing TEMPO-terminated oligomers of polystyrene (TTOPS) as the initiating species. The miniemulsion polymerization rate without TTOPS was faster than those containing TTOPS. Increasing the concentration of TTOPS from 5% to 20% had no significant effect on the miniemulsion polymerization rate. Up to 80% conversion, the molecular weight of the polymer increased almost linearly with conversion. The slope of the molecular weight vs conversion curve increased with decreasing concentration of TTOPS, as expected. However, this increase was lower than predicted from the initial number of chains added, indicating an increased number of chains and/or a population of low molecular weight dead polymer. The molecular weight polydispersities of the polymers obtained from these living free radical miniemulsion polymerizations of styrene were relatively narrow (mainly between 1.2 and 1.7, while the molecular weight polydispersities of the polymer from the control experiment without TTOPS or TEMPO varied from 2.5 to 3.2) and increased with conversion. In the miniemulsion polymerization system with the lower TTOPS concentration (5%), the molecular weight distribution broadened more with increasing conversion than the polymerization employing 20% TTOPS.

Broad latex particle size distributions were measured by both TEM and CHDF. This is not unexpected for a miniemulsion prepared in the manner described here. Large off-size particles were observed, resulting in multiple peaks and irreproducibility of the weight distribution. The values of $\bar{n}$ in these miniemulsion polymerizations were estimated using the conversion−time kinetic data. Low $\bar{n}$ values were found for the living free radical miniemulsion polymerizations ($\bar{n}_{\max} = 4.3 \times 10^{-3}$) as well as the control experiment (0% TTOPS), although the latter were an order of magnitude larger ($\bar{n}_{\max} = 2.6 \times 10^{-2}$).

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References and Notes

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