Macromolecules **2001,** *34,* 5501−5507

Theoretical Aspects of Particle Swelling in Living Free Radical Miniemulsion Polymerization

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Received December 5, 2000; Revised Manuscript Received May 21, 2001

ABSTRACT: Living free radical reactions originally were carried out in bulk or solution. Recently, this chemistry has been carried out in water-based systems (emulsion and miniemulsion living free radical polymerization). Significant colloidal instability early in the polymerization has been found in several of these systems. With the hypothesis that something unique to living free radical polymerization was causing colloidal instability beyond that found in conventional free radical emulsion polymerization, the swelling of polymer particles during the early stages of living free radical miniemulsion polymerization was investigated. A new superswelling state caused by the presence of a large number of oligomers was found. This superswelling could be used to explain the instability issues reported. The effect of various factors on the superswelling state was studied. It was found that superswelling state is rather sensitive to recipe variations. Simply increasing the costabilizer level and/or using a nonionic polymeric surfactant would probably eliminate superswelling and hence the instability.

Introduction

Living free radical polymerization has been shown to be a viable method for the synthesis of polymers with well-controlled molecular structure.[1,2] Many studies have been carried out on homogeneous living free radical polymerization based on various control mechanisms such as nitroxide-mediated living polymerization,[3−7] degenerative transfer,[8] atom transfer living polymerization,[9−12] and reversible addition fragmentation polymerization.[13] Most recently, much effort has been put into carrying out living free radical polymerization in water-based conventional emulsion (macroemulsion) or miniemulsion systems.[14−19] However, macroemulsion polymerization has not been particularly successful due to issues of mass transfer of the molecular weight control agent (RAFT, nitroxide, etc.). Miniemulsion polymerization has been proved a better alternative in terms of polymer structure control[20−26] due to its relative lack of mass transfer effects and stable particle number.

In a miniemulsion polymerization, the initial droplet size is at least 1 order of magnitude smaller than that produced in conventional emulsion polymerization. As a result, radical entry into the droplets becomes the dominant particle nucleation mechanism.[27] Ideally, the final polymer latex should be a copy of the initial miniemulsion in terms of particle size and distribution.[28] In the ideal case, this would eliminate the need for mass transfer of monomer across the aqueous phase from the monomer droplets to the polymer particles. It also allows the use of molecular weight control agents that are highly water insoluble. In conventional free radical polymerization, oligomers are formed throughout the polymerization and very rapidly grow into macromolecules. However, in living free radical polymerization, ideally, all of the oligomers are formed early in the reaction and then grow slowly into macromolecules. Ugelstad and co-workers[29,30] have shown theoretically and experimentally that oligomers are very effective swelling agents and can cause high swelling of polymer particles with monomer, whereas high polymer is a much less effective swelling agent. This paper will investigate this oligomer effect and hopefully add insight into the disperse-phase living free radical polymerization.

Theoretical Model

In miniemulsion polymerization, an effective surfactant/costabilizer system is used to stabilize very small monomer droplets (50−500 nm). To break up monomer droplets to such size, high shear is applied by sonication or homogenization. The *costabilizer* (also known as a *cosurfactant* or *hydrophobe*) is a highly monomer-soluble, highly water-insoluble material added to increase diffusional stability of the emulsion. (The costabilizer functions as a hydrophobe, but other components of the recipe may be hydrophobic as well. The term cosurfactant is not really correct, since it often has no surface activity. Here the term costabilizer will be used to distinguish it from oligomeric hydrophobes generated during the polymerization, which have a similar effect on swelling.) Usually long-chain alkanes such as hexadecane or long-chain alcohols such as cetyl alcohol are employed as costabilizers. Because these costabilizers cannot diffuse readily through the aqueous phase (due to their extremely low water solubility), removing monomer from a small monomer droplet will cause an increase in the concentration of the costabilizer, with a resultant increase in the free energy. Therefore, the use of a costabilizer will significantly retard, or even prevent Ostwald ripening (transfer of monomer from small droplets to large droplets to reduce the total surface energy of the system), and thus keep the small droplets stable during polymerization. Adequate surfactant is used to prevent colloidal instability due to coalescence.

For the sake of simplicity, in this work a *droplet* is considered to be composed only of a single monomer and costabilizer. In a *particle*, a portion of the monomer has converted into polymer. Because of the nature of living free radical polymerization, at low monomer conversions this polymer will exist almost exclusively in the form of short oligomers. The Ugelstad modification to the Morton equation[29,30] has been used to describe the

10.1021/ma0020741 CCC: $20.00

swelling of polymer particles with monomer.[31] It also has been successfully used to explain the role of costabilizer and the superswelling capacity of a particle composed of polymers and oligomers.[30] In the following, this equation will be used to analyze the scenarios in the very beginning of a living free radical miniemulsion polymerization.

From Ugelstad's equation,[30] the chemical potential of monomer droplets is determined by

$$\mu_d = RT\left(\ln \Phi_{d1} + \left(1 - \frac{1}{j_2}\right)\Phi_{d2} + {\Phi_{d2}}^2\chi_{12} + \frac{2v_1\gamma}{r_d RT}\right) \quad (1)$$

Before the start of polymerization, the chemical potential of the monomer in all droplets is equal because the monomer (for the sake of the current argument) has at least limited solubility in the aqueous phase. However, once a monomer droplet is initiated, a part of the monomer will polymerize into oligomers, and the droplet is converted into a particle. The particle chemical potential is described by[30]

$$\mu_p = RT\left[\ln \Phi_{p1} + \left(1 - \frac{1}{j_2}\right)\Phi_{p2} + \left(1 - \frac{1}{j_3}\right)\Phi_{p3} + {\Phi_{p2}}^2\chi_{12} + {\Phi_{p3}}^2\chi_{13} + \Phi_{p2}\Phi_{p3}\left(\chi_{12} + \chi_{13} - \frac{\chi_{23}}{j_2}\right) + \frac{2v_1\gamma}{r_p RT}\right] \quad (2)$$

In the above two equations, the last term of the right side is the contribution of the interfacial energy, and the remainder represents the contribution of the mixing energy. The chemical potential of monomer in the particles is lower than that in the droplets, so that the monomer in the droplets will diffuse across the aqueous phase and into the particles. For the living free radical polymerization,[2] in eq 2, on the basis of the definition of j_3, it reasonable to assume that j_3 should be proportional to the degree of polymerization of oligomers, and the proportionality should be approximately unity.

$$j_3 = k_1\overline{\mathrm{DP}}_n = k\frac{x}{f_1} \quad (3)$$

If one assumes that y weight percent of the droplets (assumed to be monodisperse) have been initiated at some time t, the swelling capacity, Y, can be defined as

$$Y = \frac{w + w_0}{w_0} \quad (4)$$

where

$$w_0 = \frac{4}{3}\pi {r_0}^3 \rho_1 \quad (5)$$

one has

$$\frac{N_p}{N_d} = \frac{y}{100 - y} \quad (6)$$

A mass balance on droplets and particles gives

$$N_d w' = N_p w \quad (7)$$

Combining eqs 4, 6, and 7, one gets

$$w' = \frac{N_p}{N_d}w = \frac{y(Y-1)w_0}{100 - y} \quad (8)$$

For the droplets,

$${r_d}^3 = {r_0}^3 - \frac{3}{4\pi\rho_1}w' \quad (9)$$

$$\Phi_{d1} = \frac{(w_0 - w')/\rho_1}{(w_0 - w')/\rho_1 + w_0 f_2/\rho_2} \quad (10)$$

$$\Phi_{d2} = 1 - \Phi_{d1} \quad (11)$$

Substituting eqs 5 and 8 into eqs 9 and 10 gives

$$r_d = \left[1 - \frac{y(Y-1)}{100 - y}\right]^{1/3} r_0 \quad (12)$$

$$\Phi_{d1} = \frac{\left(1 - \frac{y(Y-1)}{100-y}\right)\frac{1}{\rho_1}}{\left(1 - \frac{y(Y-1)}{100-y}\right)\frac{1}{\rho_1} + \frac{f_2}{\rho_2}} \quad (13)$$

For the particles,

$$r_p = \left(Y - x + \frac{x\rho_1}{\rho_3} + \frac{f_2\rho_1}{\rho_2}\right)^{1/3} r_0 \quad (14)$$

$$\Phi_{p1} = \frac{(Y-x)/\rho_1}{(Y-x)/\rho_1 + f_2/\rho_2 + x/\rho_3} \quad (15)$$

$$\Phi_{p2} = \frac{f_2/\rho_2}{(Y-x)/\rho_1 + f_2/\rho_2 + x/\rho_3} \quad (16)$$

$$\Phi_{p3} = 1 - \Phi_{p1} - \Phi_{p2} \quad (17)$$

Simulation Parameters and Conditions. All simulations were made for methyl methacrylate as the monomer and hexadecane as the costabilizer. The parameters are[32] $\chi_{12} = 1.28$, $\chi_{13} = 0.465$, $\chi_{23} = 3.359$, $j_2 = 1.292$, $v_1 = 1.0994 \times 10^{-4}$ m^3/mol, $\rho_1 = 78.5678/0.25327^{(1+(1-T/564.0)^{0.28571})}$, $\rho_2 = 61.944/0.25442^{(1+(1-T/720.6)^{0.3238})}$, $\rho_3 = 1188/(1 + 2.55 \times 10^{-4}(T - 298.15))$, and $R = 8.31$ J/(K mol).

Unless otherwise indicated, simulations were made under the following conditions, which are typical in miniemulsion polymerization: $r_0 = 60$ nm, $y = 0.01$, $\gamma = 0.025$ N/m, $T = 323.15$ K, $f_2 = 0.02$, $f_I = 0.01$, and $x = 0.1$

Simulation Results and Discussion

Properties of the Chemical Potential of the Monomer. In Figure 1, a typical plot of monomer chemical potential vs particle swelling is shown. It is clear that once a droplet is nucleated, its monomer chemical potential drops and is lower than that of the unnucleated droplets. Because of this, monomer will diffuse from the higher chemical potential droplets to the lower chemical potential particles. With monomer diffusion (increase in Y), particles swell. Swelling leads to two effects: first, a decrease in the interfacial energy caused by an increase in particle size, and second, a dilution of the oligomer concentration particles. The first effect decreases and the second effect increases the

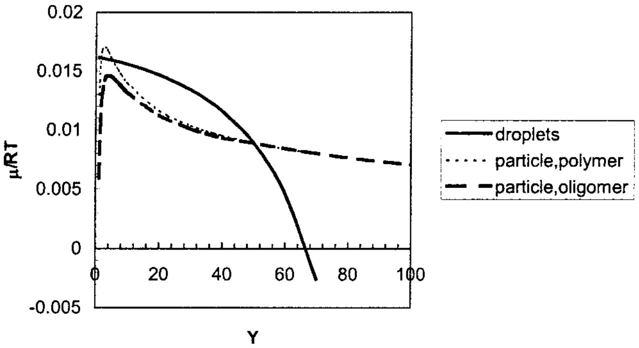

Figure 1. General description of the chemical potential of droplets and particles during particle swelling.

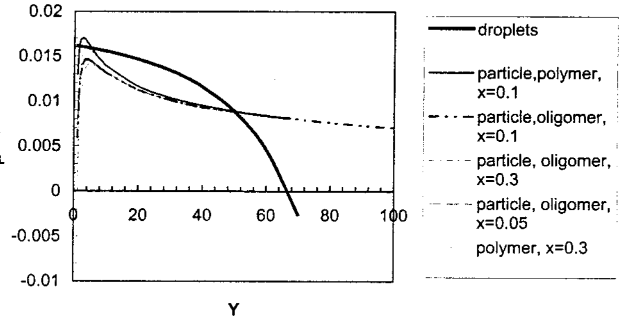

Figure 2. Effect of monomer conversion on the monomer chemical potential vs swelling ratio of particles. $r_0 = 60$ nm.

chemical potential. At low Y the second effect prevails whereas at high Y the first effect dominates. As a result, the chemical potential of monomer in the particles first increases rapidly and then decreases gradually down to zero with more and more monomer swelling. The droplets, on the other hand, shrink, and the costabilizer is concentrated since it cannot (by definition) diffuse out with the monomer. The decrease in the mixing energy is dominant so that the monomer chemical potential decreases monotonically.

During the process of monomer diffusion, if the monomer chemical potential in the droplets is equal to that of the particles, equilibrium is established and monomer diffusion ceases. In Figure 1, a case with formation of high polymer, three intersections of the droplet and particle chemical potential curves can be seen. Two of these occur at low Y and the third at a much higher Y. As is often the case with three equilibrium points, the middle point is unstable. When the system arrives at the first intersection during swelling (lowest Y), monomer transfer stops, and the system comes to an equilibrium state which will be denoted as the *normal swelling state*. In this case, the other two equilibrium points would never be reached. However, in the case of living polymerization, the formation of oligomers rather than high molecular weight polymer leads to a lower mixing free energy so that the monomer in the particles has a lower chemical potential. If the effect is large enough so that the chemical potential of the droplets remains higher than that of the particles at the peak of the chemical potential curve of particles, the system will go to the rightmost equilibrium point. This will be denoted as the *superswelling state*. In this case, a large amount of monomer would transfer from the droplets to the particles, causing colloidal instability. Clearly, it is important to investigate the effects of various process and recipe parameters on the existence of the superswelling state.

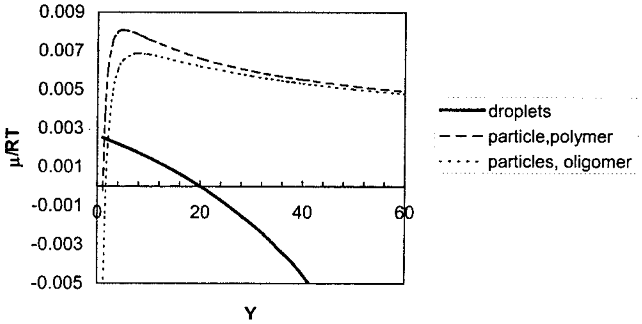

Figure 3. Monomer chemical potential of droplets and particles in the particle swelling process. $r_0 = 100$ nm.

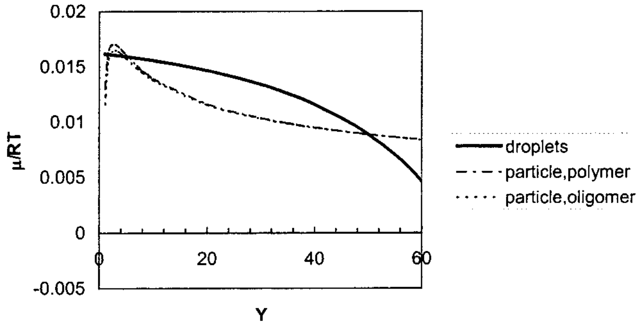

Figure 4. Monomer chemical potential vs swelling ratio of particles at a molecular weight controlling compound level of $f_1 = 0.002$.

Effect of Monomer Conversion in the Particles. In Figure 2, the effect of monomer conversion in the particles on the chemical potential curves is shown. It is clear that with an increase in conversion the monomer chemical potential in the particles deceases in the low-Y region but is little affected at high Y because the mixing energy is only significant at low Y. In comparison with the case of formation of high polymer (Figure 1), the effect of monomer conversion is much less in the case of the living polymerization. That is because with increasing conversion, molecular weight of the oligomers also increases, partially offsetting the effect of an increase in the oligomer volume fraction. It should be pointed out that the monomer conversion here is based on the initial amount of monomer in a particle. From these equilibrium considerations, when the conversion is high enough, superswelling could occur even in normal miniemulsion polymerization; however, as will be discussed later, kinetic considerations preclude that possibility.

Effect of Droplet Size. In Figure 3, the droplet radius is set to 100 nm. This plot may be compared with Figure 2 where the droplet radius is 60 nm and all other conditions are identical. It may be seen that the droplet chemical potential curve drops more than that of the particles, so that the superswelling equilibrium state in Figure 2 does not exist in Figure 3.

Effect of Concentration of Molecular Weight Control Agent. If the concentration of the molecular weight control agent is decreased, the situation is shown in Figure 4. The chemical potential curve of the particle moves upward. Here there are three crossing points just as in the situations without the molecular weight controlling agent. During swelling, only the first point can be reached, and so superswelling would not be observed.

Effect of Costabilizer Level. If the hexadecane level is increased from 2 wt % (based on monomer) in

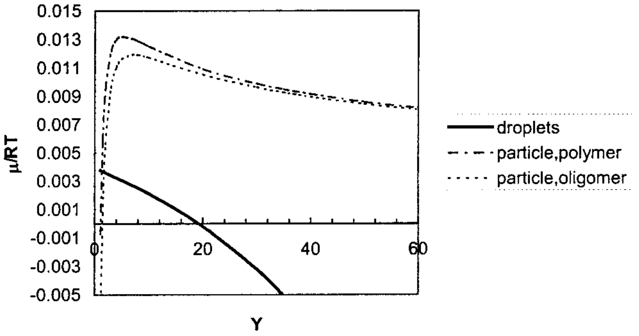

Figure 5. Monomer chemical potential vs swelling ratio of particles at a costabilizer level of $f_2 = 0.035$.

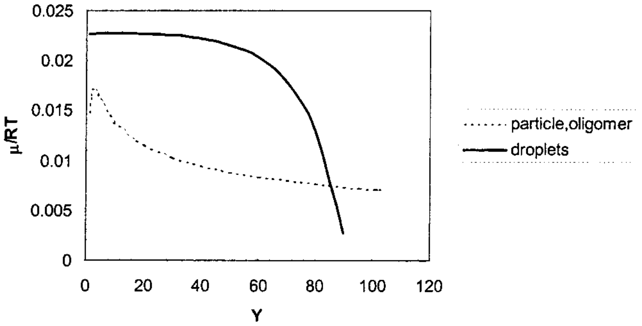

Figure 6. Monomer chemical potential vs swelling ratio of particles with $j_2 = 2$.

Figure 2) to 3.5 wt % in Figure 5, the chemical potential curve of the droplets drops because of the lower mixing free energy. However, the lower mixing free energy is partly offset by the dilution effect in the case of particles. As a result, the superswelling state reverts to the normal one.

Effect of Length of Costabilizer. Ugelstad and coworkers[30] have stated that an effective costabilizer must have two properties, namely a very high degree of water insolubility and a relatively low molecular weight. However, it has been shown that even polymer can be used as a costabilizer.[33] It is interesting to investigate the effect of the length of costabilizer. In Figure 6, j_2 in eqs 1 and 2 is adjusted from 1.292 to 2. It is found that the two curves intersect at a much higher swelling ratio. At the peak position of the particle curve, the chemical potential difference between droplets and particles is much larger than that in Figure 2. As is discussed later, this means that the system is more likely to get to the superswelling state.

Kinetic Considerations. In the above simulations, the monomer chemical potential in the particles and droplets are statically computed as a function of the swelling state of the particles. Clearly, kinetics should be considered. During polymerization, an increasing number of droplets are converted to particles. The effect of the number ratio of particles to droplets is shown in Figure 7. It may be found that, for the higher number ratio of particles to the droplets, the potential of the droplets decreases faster with an increase in the swelling ratio. This leads to a much lower equilibrium swelling capacity. This indicates that the nucleation process has a large influence on the existence of the superswelling state. The establishment of the superswelling state depends on the relative rate of monomer transfer and nucleation. There have been reports that nucleation in miniemulsions is rather slow.[34] If monomer transport is relatively slow, the superswelling state would be depressed because of the formation of new particles. For an example, using nonionic polymeric surfactant would probably hinder monomer transport so that it would be less likely that the superswelling would occur. If the transport through the aqueous phase is rate determining, the rate of transport of monomers is given by[30]

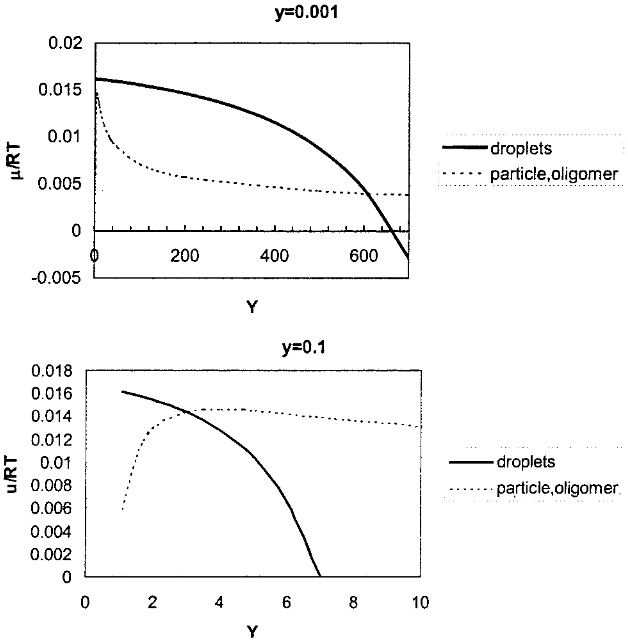

Figure 7. Effect of the ratio of particles to droplets on the monomer chemical potential vs swelling ratio of particles.

$$\frac{\mathrm{d}w}{\mathrm{d}t} = \frac{4\pi D_{\mathrm{w}} N_{\mathrm{p}} N_{\mathrm{d}} r_{\mathrm{d}} r_{\mathrm{p}} C_{\mathrm{m}} (\exp(\mu_{\mathrm{d}}/RT) - \exp(\mu_{\mathrm{p}}/RT))}{N_{\mathrm{p}} r_{\mathrm{p}} + N_{\mathrm{p}} r_{\mathrm{p}}} \tag{18}$$

From this equation, for a system with a large difference in chemical potential, somewhat water-soluble monomer, and a high diffusion coefficient, the superswelling state would be more likely occur. From the above simulations, it is found that the difference in monomer chemical potential (between droplets and particles) is the smallest near the peak of the chemical potential curve vs particle swelling. Once passed the peak, the swelling would occur more quickly. This means that the swelling could be a very rapid process.

Another dynamic property is the interfacial tension. In the swelling process, the interfacial tension would not be constant as is assumed in the above simulations because of variation in the surface area. As shown in Figure 8, if the interfacial tension is adjusted from 25 to 20 mN/m, the superswelling would disappear. The change of interfacial tension is inversely proportional to the variation of total surface area, which is very much influenced by the initial droplets size distribution.

Consequences of the Superswelling Equilibrium. For a living free radical miniemulsion polymerization, it is desirable that a droplet be an isolated microreactor to keep the polymerization controlled. However, it has been shown that in miniemulsion polymerization nucleation is a slow process. Additionally, most monomers have a sufficient water solubility to be able to transport between droplets and particles. Transport of monomer or other components in the droplets and particles from a higher chemical potential locus to a lower chemical potential locus is unavoidable.

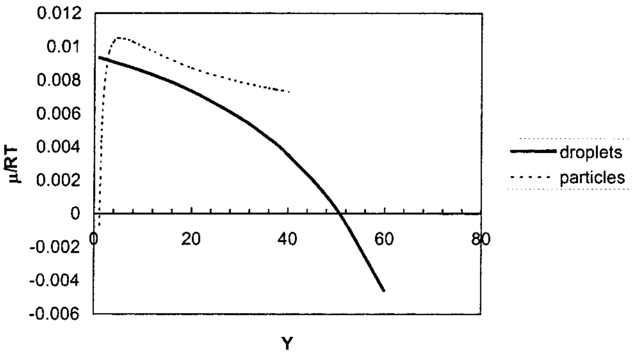

Figure 8. Monomer chemical potential vs swelling ratio of particles with an interfacial tension of 0.02 N/m.

It is evident that even in the traditional miniemulsion polymerization, this kind of mass transfer would lead to deviation from the ideal situation.[35] As shown here, in the case of the living free radical miniemulsion polymerization, the situation is much more complicated. The system becomes rather sensitive. In some cases, the particles show the normal swelling equilibrium which does not disturb the polymerization. However, in other cases, the particles can go to a superswelling equilibrium state.

During approach to the superswelling equilibrium point, a large amount of monomer would transfer from a large number of droplets to a small number of particles, which would cause the monomer droplets to shrink and particles to swell. First, this would broaden the particle size distribution or even to destroy the miniemulsion. In the worst case, the superswelling would lead to a very large size difference between the droplets and particles. The particles could be swollen to around 1 μm, a critical size where the system become shear sensitive and buoyant forces dominate. Because in a miniemulsion polymerization reactor shear is low, the particles would rapidly approach a breaking–coagulating dynamic balance particle size, as in suspension polymerization. In this case, particle size could be more than 10 μm or even form a bulk phase, depending on the shear fielded. Alternatively, it is possible to destroy the miniemulsion by the so-called heterocogualation (small particles/droplets coagulating onto large ones) when the size difference becomes large. Second, it would cause a composition distribution among the particles so that the molecular weight and its distribution would deviate from the theory of living polymerization or even could not be controlled.

Application to Literature Reports. Recently, issues of the stability of the latex in living free radical miniemulsion polymerization have been reported in several papers. De Brouwer et al.[23] reported stability problems in living free radical miniemulsion polymerization using RAFT. It is reported that when an ionic surfactant (either cationic or anionic) was used, a monomer bulk phase constituting up to 35% of the total organic material in the system could be observed at low monomer converison. It is noted that the phenomenon is seen with various different monomers, different initiator systems, and different costabilizers. Until now, no satisfactory explanation has been available. However, Figure 7 simulates the situations in question. In the case of the ratio of particles to droplets of 1/999, particles with 5% monomer conversion would swell to more than 600 times their original weight. In an equilibrium state, the particle diameter would arrive at 0.45 μm with a composition of more than 60 wt % monomer. It is well-known that when particles are approaching 1 μm, the system becomes shear sensitive and buoyant force dominate. This agrees with de Brouwer's observation that the organic layer first occurred in the vortex of the stirred miniemulsion, where shear forces are strongest. De Brouwer found that when nonionic surfactant is used, the polymerization is well controlled in molecular weight and the colloidal stability is good. It is well-known that nonionic surfactants are less efficient than ionic surfactants and result in much larger droplets.[36] It is reported that the average radius of the final latex particles is greater than 80 nm. According to the above simulation, in the case of larger droplet size, the superswelling state is less likely. The other advantage of nonionic surfactants is that they are usually polymeric, which would hinder monomer transfer.[34] Hindrance of monomer transfer could be an effective way to suppress the superswelling as discussed previously.

Table 1. Summary of Georges and Co-workers' Results for TEMPO[38]

	case 1	case 2	case 3
surfactant concn, wt %	0.35	1.4	0.7
hexadecane concn, wt %	0.9	3.6	3.6
TEMPO:KPS ratio	1.2:1	2.4:1	2.9:1
living level	nonliving	partially living	living
instability of miniemulsion	stable	nonstable	stable

Matyjaszewski et al.[37] have studied the ATRP living free radical miniemulsion polymerization and found that using either anionic (sodium lauryl sulfate) or cationic (dodecyltrimethylamomonium bromide) surfactant led to instability. The final particle size was more than 1 μm in the normal ATRP polymerization of butyl methacrylate and more than 250 nm in reverse ATRP. It has been reported that using nonionic polymeric surfactant improved the stability. Also, the longer the PEO segment in the surfactant was, the better the stability. In the case of Tween 20, a portion of the monomer phase separated, forming small pools in the reaction mixture, but these would dissipate as the polymerization progressed, and there was no coagulation of polymer at higher conversion. All these phenomena can be well justified by the above simulations and discussions.

In another paper,[38] Georges and co-workers reported miniemulsion polymerization of nitroxide living polymerization. This system showed rather sensitive to recipe variations. The results are summarized in Table 1. It is interesting to compare case 2 and case 3. In case 3, the surfactant concentration was reduced by one-half and the TEMPO:KPS ratio was increased from 2.4:1 to 2.9:1. Case 2 was unstable, had a bimodal distribution of particles, and was only partially living, whereas case 3 was stable with a monomodal particle distribution and good living character. The change of TEMPO should have little influence on the stability of the miniemulsion because the miniemulsion was initially stable. According to the present simulation, we could easily ascribe the stability and living nature of case 3 to the increase the initial droplet size resulting from the reduced surfactant level. As shown in Figure 3, the increased droplet size would depress the superswelling. (It can be inferred roughly from the paper that the initial droplet size is around 30 nm for case 2 and 50 nm for case 3.)

El-Aasser[39] reported successful miniemulsion polymerization employing nitroxides with controlled molecular growth and good miniemulsion stability. It is interesting to note that the level of costabilizer was more than 5 wt %, far more than the typical 2 wt %. It has been shown here that a high level of costabilizer can be used to depress superswelling. Even so, El-Aasser's particle size was much larger than the nonliving counterpart and the particle size distribution much broader.

In two additional papers on living free radical miniemulsion polymerization,[21,22] a degenerative transfer agent (C6F13I) was used to control molecular weight. It was reported that the final latex morphology was well controlled. C6F13I is not a very efficient transfer agent (C_{tr} = 1.4 at 70 °C), so that at the beginning of polymerization the degree of polymerization of the product was rather high. As shown in the simulations above, superswelling is less likely to occur in such a case.

Conclusions

The literature cited here indicates that instability is a general problem in living free radical miniemulsion polymerization, regardless of the living control mechanism, monomer, surfactant system (except for polymeric surfactant), or initiator system. The only feature common to all of these systems is the presence of large concentrations of oligomers early in the polymerization. This strongly supports the idea that the instability is caused by a thermodynamic mechanism such as the superswelling of the particles. From the above simulations, one can safely conclude that in specific cases superswelling will occur in the living miniemulsion polymerization if the very low molecular weight oligomers are formed at the very beginning of polymerization. Superswelling is more likely in a system with slow nucleation and fast monomer transport. Increasing the costabilizer level or using a polymeric surfactant is shown to be an efficient way to avoid superswelling.

Nomenclature

C_m	solubility of monomer in the aqueous phase from a plane surface consisting of pure monomer
$\overline{DP}_n$	number-average degree of polymerization
D_w	diffusion coefficient of monomer in the aqueous phase
f_2	initial weight ratio of costabilizer to monomer in a particle
f_I	molar ratio of the molecular weight controlling agent to monomer
j_i	ratio of the molar volume of compound *i* to that of monomer
k	proportionality constant
N_a	no. concentration of phase *a* (droplet or particle)
r_0	radius of the initial droplets
r_a	radius of phase *a*
R	gas constant
T	temperature
x	fractional monomer conversion in a particle based on the initial monomer amount of a particle
v_1	molar volume of monomer
w_0	initial mass of monomer in a particle
w	mass of monomer absorbed by a particle by swelling
w'	mass of monomer lost by a droplet due to particle swelling
y	weight percent of droplets that have been nucleated

Greeks

μ_a	monomer chemical potential of *a*
ρ_1	density of the monomer
Φ_{ai}	vol fraction of compound *i* in phase *a*
γ	interfacial tension
χ_{ij}	compound *i* and *j* interaction parameter
ρ_i	density of compound *i*

Subscripts

0	initial
1	monomer
2	costabilizer
3	oligomer
d	droplets
p	particles

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MA0020741