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Synergistic Effects of Compartmentalization and Nitroxide Exit/Entry in Nitroxide-Mediated Radical Polymerization in Dispersed Systems

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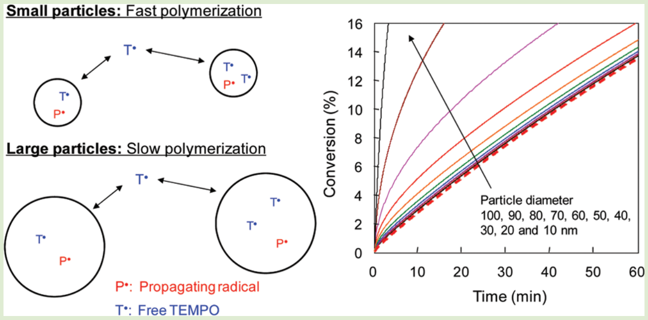
Supporting Information

ABSTRACT: Modeling and simulations of compartmentalization effects in tandem with nitroxide exit and entry have been performed for the nitroxide-mediated radical polymerization (NMP) of styrene in an aqueous dispersed system employing 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) at 125 °C. It is demonstrated that, even for a relatively water-insoluble nitroxide like TEMPO, exit and entry can strongly influence the polymerization kinetics in submicrometer-size droplets/particles. In such systems, the polymerization is expected to proceed at a markedly higher rate than the corresponding bulk system at the expense of control/livingness. Depending on the deactivator water solubility, these findings will apply qualitatively to all controlled/living radical polymerization systems governed by the persistent radical effect [e.g., NMP and atom transfer radical polymerization (ATRP)].



Controlled/living radical polymerization (CLRP)[1] was initially developed for homogeneous polymerization systems, but the past decade has seen significant progress in (aqueous) dispersed systems.[2] There are a number of intrinsic characteristics of such dispersed systems, for example, reactant partitioning and phase transfer events[3] and interface[4] and compartmentalization effects,[5] and the polymerization may proceed quite differently compared to its homogeneous counterpart. Ultimately, one strives to understand and exploit these phenomena to further improve the efficiency of the process in terms of control of the molecular weight distribution (MWD) and the "livingness" (end-functionality).[6]

Compartmentalization refers to the confinement of reactants within discrete confined spaces (nanoreactors). A number of theoretical studies of compartmentalization effects in CLRP have been reported, using either modified Smith–Ewart equations[5–7] or Monte Carlo modeling.[8] In nitroxide-mediated radical polymerization (NMP)[6a,7c,f,h–j,n,p,8g,9] and atom transfer radical polymerization (ATRP),[6b,7d,g,k,m,8c,g] both the propagating radicals and deactivator may be compartmentalized, and consequently not only bimolecular termination but also the deactivation reaction may be influenced by compartmentalization. However, the above studies all deal with the situation where the deactivator is unable to exit into the aqueous phase (or where the deactivator is not compartmentalized[7b]). Although such systems undoubtedly exist (e.g., when using a polymeric nitroxide[4a]), deactivator partitioning will occur to various extents in most systems. Bentein et al.[7p] simulated *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1)-mediated radical polymerization of styrene (St) in miniemulsion at 123 °C with modified Smith–Ewart equations with nitroxide exit/entry modeled using a semiempirical approach for a particle diameter of 70 nm. Not surprisingly, under such conditions (i.e., an NMP system with high equilibrium constant and "large" particles), no strong effects of nitroxide partitioning were observed due to the high number of SG1 species per particle (~40).

In the present work, modeling and simulations of compartmentalization effects in tandem with nitroxide exit and entry have been performed for the NMP system St/2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO)/125 °C. It is demonstrated that even for a relatively water insoluble nitroxide like TEMPO, exit and entry can strongly influence the polymerization kinetics in submicrometer-size droplets/particles.

Modeling and simulations were conducted using Smith–Ewart equations accounting for the compartmentalization of propagating radicals and nitroxide,[7a,c] as well as the exit/entry of nitroxide:

$$\begin{aligned}\frac{dN_i^j}{dt} &= (N_\mathrm{A}v_\mathrm{p})k_\mathrm{act}[\mathrm{PT}](N_{i-1}^{j-1} - N_i^j) + \frac{k_\mathrm{deact}}{(N_\mathrm{A}v_\mathrm{p})}\\ &\times \{(i+1)(j+1)N_{i+1}^{j+1} - ijN_i^j\} + (N_\mathrm{A}v_\mathrm{p})0.5k_\mathrm{i,th}\\ &\times [\mathrm{M}]^3(N_{i-2}^j - N_i^j) + \frac{k_\mathrm{t}}{(N_\mathrm{A}v_\mathrm{p})}\{(i+2)(i+1)N_{i+2}^j\\ &- i(i-1)N_i^j\} + (N_\mathrm{A}v_\mathrm{w})k_\mathrm{entry}[\mathrm{T}^\bullet]_\mathrm{w}(N_i^{j-1} - N_i^j)\\ &+ k_\mathrm{exit}\{(j+1)N_i^{j+1} - jN_i^j\} \qquad (1)\end{aligned}$$

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where N_A is Avogadro's number, v_p the droplet/particle volume, v_w the volume of the continuous phase, and k_{act}, k_{deact}, $k_{i,th}$, k_t, k_{entry}, and k_{exit} are the rate coefficients for alkoxyamine activation, deactivation, thermal initiation of styrene, termination, entry, and exit, respectively (see the Supporting Information (SI) for a complete model description). Nitroxide exit/entry was modeled using a previously developed theory[10] in connection with the experimentally obtained partitioning coefficient of TEMPO between St/water at 135 °C; $\Gamma = [\mathrm{TEMPO}]_{St}/[\mathrm{TEMPO}]_{water} = 98.8$.[11] The model corresponds to an ideal miniemulsion polymerization comprising monodisperse monomer droplets, where each droplet is converted to a polymer particle.

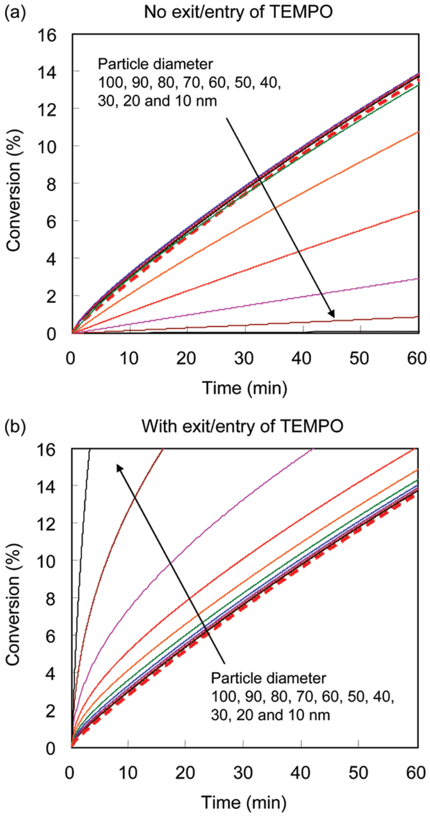


Figure 1. Simulated conversion−time data for NMP of styrene using St-TEMPO initiator at 125 °C (a) without and (b) with exit/entry of TEMPO at various particle diameters ($[\mathrm{St}]_0/[\mathrm{St\text{-}TEMPO}]_0 = 8.71{:}0.02$). Broken lines denote simulated bulk NMP.

All simulations correspond to the system St/TEMPO/125 °C ($[\mathrm{alkoxyamine}]_0 = 0.02$ M). It should be noted that particle diameters below ~50 nm correspond to microemulsion polymerizations, emulsion polymerizations at very low conversion, and miniemulsion systems with exceptionally small particles. Figure 1a shows simulations in the absence of exit/entry of TEMPO, revealing how the rate of polymerization (R_p) decreases with decreasing particle size in agreement with previous theoretical works.[7c] Now, accounting for exit/entry of TEMPO results in completely different trends: R_p increases markedly with decreasing particle size (Figure 1b). The dramatic effect of TEMPO partitioning on R_p is further examined in Figure 2, which shows overlays of conversion−time data with and without exit/entry and the corresponding homogeneous (bulk) system for diameters 10, 40, and 70 nm. For the smallest diameter of 10 nm, there is an enormous difference in R_p with and without exit/entry. The difference is less dramatic for 40 nm, and both systems exhibit R_p similar to in bulk for 70 nm.

The "livingness" (end-group fidelity) can be assessed by the examination of the ratio of alkoxyamine chain ends relative to the initial amount ($[\mathrm{PT}]/[\mathrm{PT}]_0$). Figure 3 shows $[\mathrm{PT}]/[\mathrm{PT}]_0$ versus conversion with and without exit/entry and the corresponding bulk system for the particle diameters 10, 40, and 70 nm. The livingness is higher for both dispersed systems than the bulk system, and this difference is more pronounced for smaller particles, and the livingness with exit/entry is lower than without exit/entry. The livingness is extremely high in all cases (in agreement with earlier theoretical work[5]), and the absolute differences in livingness between the different cases are very small, suggesting that the practical relevance may be limited. It should also be mentioned that a significant fraction of the original alkoxyamine initiator would be remaining (i.e., not yet chain-extended) at 10% conversion (especially for small particles, as they exhibit higher R_p).

It is not possible to compute the MWD using the present model, but the influence of compartmentalization on the MWD can be examined by inspection of the number of monomer units added per chain per activation−deactivation cycle (ν), which is given by:[7c]

$$\nu = \frac{k_p[\mathrm{M}][\mathrm{P}^\bullet]}{(N_A v_p)^{-2} k_{deact} \sum_i \sum_j ij N_i^j} \tag{2}$$

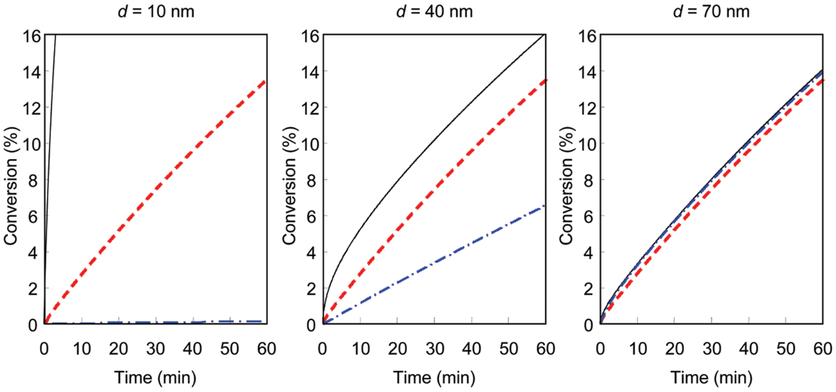


Figure 2. Simulated conversion−time data for NMP of styrene using St-TEMPO initiator at 125 °C without (blue broken-dotted lines) and with (black solid lines) exit and entry of TEMPO at particle diameters of 10 (left), 40 (center), and 70 nm (right) ($[\mathrm{St}]_0/[\mathrm{St\text{-}TEMPO}]_0 = 8.71{:}0.02$). The red broken lines denote simulated bulk NMP.

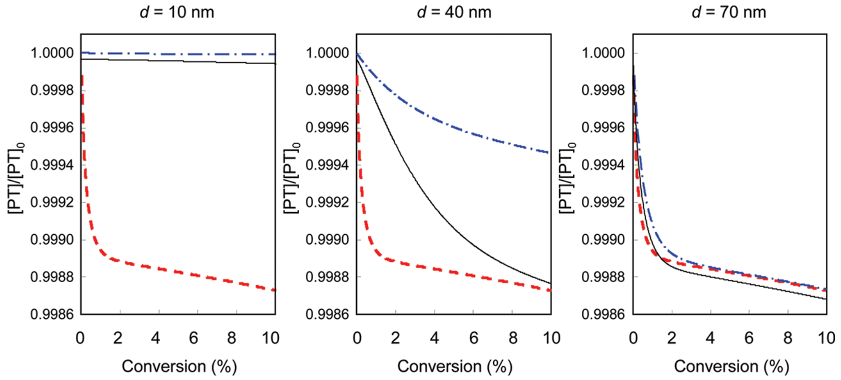
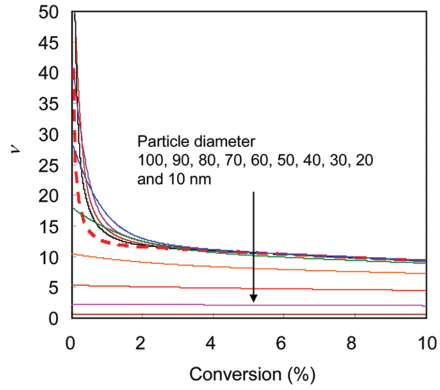


Figure 3. Simulated values of number fraction (relative to the initial amount) of alkoxyamine as a function of conversion for NMP of styrene using St-TEMPO initiator at 125 °C without (blue broken-dotted lines) and with (black solid lines) exit and entry of TEMPO at 10 (left), 40 (center), and 70 nm (right) ($[\mathrm{St}]_0/[\mathrm{St\text{-}TEMPO}]_0 = 8.71{:}0.02$). The red broken lines denote simulated bulk NMP.

For a given molecular weight, the polydispersity (M_w/M_n) decreases with decreasing ν (all other parameters being constant). Figure 4 shows ν versus conversion with and without exit/entry, revealing how exit/entry dramatically alters the behavior of the system. In the case of exit/entry, ν is larger than in bulk and increases with decreasing particle size, that is, the exact opposite to the behavior without exit/entry. Figure 5 shows ν versus conversion for the systems with and without exit/entry as well as bulk for the particle diameters 10, 40, and 70 nm. There are only minor differences between the systems at 70 nm (particles too large for compartmentalization effects to be strong), whereas ν(no exit/entry) < ν(bulk) < ν(exit/entry) for 40 and 10 nm (for 10 nm, both dispersed systems give ν values off scale). The very high values of ν in the case of exit/entry for small particles can be explained by considering that an activation event in a particle that contains no propagating radicals and no nitroxide (which is the case for the vast majority of particles) results in a particle containing one propagating radical and one nitroxide. Now, the exit/entry of nitroxide means that this nitroxide may exit and nitroxide may also enter from the aqueous phase. The net result is that the time during which the propagating radical exists alone in the particle is prolonged, thus effectively reducing the deactivation rate and resulting in a high value of ν.


(a) No exit/entry of TEMPO

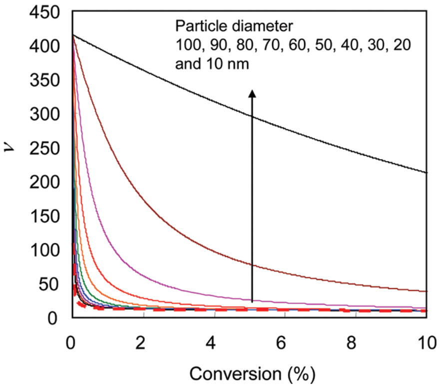

(b) With exit/entry of TEMPO

Figure 4. Simulated number of propagation events per activation–deactivation cycle for an individual chain (ν) vs conversion for NMP of styrene using St-TEMPO initiator at 125 °C (a) without and (b) with exit/entry of TEMPO at various particle diameters ($[\mathrm{St}]_0/[\mathrm{St\text{-}TEMPO}]_0 = 8.71{:}0.02$). Broken lines denote simulated bulk NMP.

The above results show that, even for a relatively hydrophobic nitroxide such as TEMPO, it is essential to consider phase transfer events. The exit/entry of TEMPO has a major effect on the system—relative to the corresponding bulk system, R_p increases, and the livingness increases, but the MWD becomes broader. This is in sharp contrast to the situation when the exit/entry of nitroxide is not considered, in which case compartmentalization leads to (relative to bulk) lower R_p, higher livingness, and narrower MWD. From a mechanistic viewpoint, the results can be explained by considering that, for a compartmentalized NMP system, the very vast majority of particles contain no propagating radicals and no nitroxide, and thus the exit of TEMPO from a particle where an activation event has occurred results in a particle containing only a propagating radical. In such a particle, uncontrolled propagating will occur (unless a TEMPO species enters from the aqueous phase or another activation event occurs), thus accounting for the increase in R_p and (partial) loss of control over the MWD (higher ν; Figure 4). A detailed, complete explanation of the above results from a mechanistic perspective will be provided in the near future in a forthcoming full paper.[12]

A survey of the literature on TEMPO-mediated polymerization of styrene in dispersed systems reveals a mixed bag of results. The majority of the miniemulsion systems studied exhibit very similar behavior as in bulk.[13] The particle diameters in such systems generally tend to be in the range 80–200 nm, which is too large for compartmentalization effects to be significant. Moreover, particle size distributions in miniemulsions are often relatively broad,[13b,14] which would reduce any effect of compartmentalization as the predominant loci of polymerization (in terms of mass of polymer formed) would be the larger

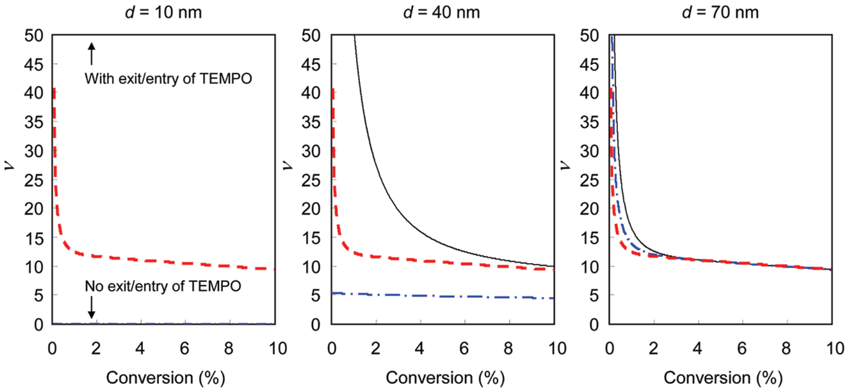


Figure 5. Simulated number of propagation events per activation−deactivation cycle for an individual chain (ν) vs conversion for NMP of styrene using a St-TEMPO initiator at 125 °C without (blue broken-dotted lines) and with (black solid lines) exit/entry of TEMPO at 10 (left), 40 (center), and 70 nm (right) ($[St]_0/[St\text{-}TEMPO]_0 = 8.71{:}0.02$). Red broken lines denote simulated bulk NMP.

particles. Maehata et al.[15] reported data consistent with compartmentalization effects without exit/entry for TEMPO-mediated miniemulsion polymerization of styrene at 135 °C using the surfactant Dowfax 8390 (d_n = 47−163 nm), whereas TEMPO-mediated miniemulsion polymerization of styrene at 125 °C using sodium dodecyl benzene sulfonate (SDBS) has been reported to proceed with higher R_p than the corresponding bulk system.[16] Nakamura et al.[4a,f] found that R_p increased and the control/livingness decreased with decreasing particle size for the TEMPO-mediated miniemulsion polymerization of styrene at 125 °C using SDBS (d_n = 70−170 nm). Other than compartmentalization effects, factors such as a rate enhancing effect of SDBS[16] as well as an interface effect (adsorption of nitroxide at the oil−water interface)[4a,f] have been put forward as possible explanations. TEMPO-mediated microemulsion polymerization of styrene at 125 °C using a radical initiator (e.g., benzoyl peroxide) and free TEMPO has also been reported by Wakamatsu et al.,[9] revealing a dramatic decrease in R_p relative to bulk. However, in light of the findings in the present study, this low R_p may have originated in an excess of free TEMPO.[7h] It is thus surmised that none of the above studies concern experimental conditions consistent with a situation where an increase in R_p and (partial) loss of control/livingness would occur as a result of compartmentalization and exit/entry of TEMPO. For this to occur, the initiating system must be an alkoxyamine with no (or very little) free TEMPO (i.e., not a radical initiator/free TEMPO system) and sufficiently small particles.

In summary, it has been shown by modeling and simulations that TEMPO-mediated polymerization of styrene in a dispersed system where compartmentalization effects are operative can be dramatically influenced by nitroxide exit/entry for sufficiently small particles. In such systems, the polymerization is expected to proceed at a markedly higher R_p than the corresponding bulk system at the expense of control/livingness. Depending on the deactivator water solubility, these findings will apply qualitatively to all CLRP systems governed by the persistent radical effect (e.g., NMP and ATRP).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full description of the model. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93−146.

(2) (a) Zetterlund, P. B.; Kagawa, Y.; Okubo, M. *Chem. Rev.* **2008**, *108*, 3747−3794. (b) Cunningham, M. F. *Prog. Polym. Sci.* **2008**, *33*, 365−398. (c) Zetterlund, P. B.; Aldabbagh, F.; Okubo, M. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 3711−3728.

(3) (a) Ma, J. W.; Cunningham, M. F.; McAuley, K. B.; Keoshkerian, B.; Georges, M. K. *Macromol. Theory Simul.* **2002**, *11*, 953−960. (b) Zetterlund, P. B.; Okubo, M. *Macromol. Theory Simul.* **2005**, *14*, 415−420. (c) Kagawa, Y.; Zetterlund, P. B.; Minami, H.; Okubo, M. *Macromolecules* **2007**, *40*, 3062−3069.

(4) (a) Zetterlund, P. B.; Nakamura, T.; Okubo, M. *Macromolecules* **2007**, *40*, 8663−8672. (b) Zetterlund, P. B.; Alam, N.; Okubo, M. *Polymer* **2009**, *50*, 5661−5667. (c) Zetterlund, P. B.; Alam, M. N.; Minami, H.; Okubo, M. *Macromol. Rapid Commun.* **2005**, *26*, 955−960. (d) Saka, Y.; Zetterlund, P. B.; Okubo, M. *Polymer* **2007**, *48*, 1229−1236. (e) Alam, M. N.; Zetterlund, P. B.; Okubo, M. *Polymer* **2009**, *50*, 1632−1636. (f) Nakamura, T.; Zetterlund, P. B.; Okubo, M. *Macromol. Rapid Commun.* **2006**, *27*, 2014−2018.

(5) Zetterlund, P. B. *Polym. Chem.* **2011**, *2*, 534−549.

(6) (a) Zetterlund, P. B. *Aust. J. Chem.* **2010**, *63*, 1195−1200. (b) Simms, R. W.; Cunningham, M. F. *Macromolecules* **2008**, *41*, 5148−5155.

(7) (a) Butte, A.; Storti, G.; Morbidelli, M. *DECHEMA Monogr.* **1998**, *134*, 497−507. (b) Charleux, B. *Macromolecules* **2000**, *33*, 5358−5365. (c) Zetterlund, P. B.; Okubo, M. *Macromolecules* **2006**, *39*, 8959−8967. (d) Kagawa, Y.; Zetterlund, P. B.; Minami, H.; Okubo, M. *Macromol. Theory Simul.* **2006**, *15*, 608−613. (e) Luo, Y.; Wang, R.; Yang, L.; Li, B.; Zhu, S. *Macromolecules* **2006**, *39*, 1328−1337. (f) Zetterlund, P. B.; Okubo, M. *Macromol. Theory Simul.* **2007**, *16*, 221−226. (g) Zetterlund, P. B.; Kagawa, Y.; Okubo, M. *Macromolecules* **2009**, *42*, 2488−2496. (h) Zetterlund, P. B.; Wakamatsu, J.; Okubo, M. *Macromolecules* **2009**, *42*, 6944−6952. (i) Zetterlund, P. B.; Okubo, M. *Macromol. Theory Simul.* **2009**, *18*, 277−286. (j) Zetterlund, P. B. *Macromol. Theory Simul.* **2010**, *19*, 11−23. (k) Zetterlund, P. B. *Macromolecules* **2010**, *43*, 1387−

1395. (l) Zetterlund, P. B. *Polymer* **2010**, *51*, 6168−6173. (m) Thomson, M. E.; Cunningham, M. F. *Macromolecules* **2010**, *43*, 2772−2779. (n) Zetterlund, P. B. *Macromol. React. Eng.* **2010**, *4*, 663−671. (o) Zetterlund, P. B. *Macromol. Theory Simul.* **2011**, *20*, 660−666. (p) Bentein, L.; D'hooge, D. R.; Reyniers, M. F.; Marin, G. B. *Polymer* **2012**, *53*, 681−693.

(8) (a) Tobita, H. *Macromol. Theory Simul.* **2007**, *16*, 810−823. (b) Tobita, H.; Yanase, F. *Macromol. Theory Simul.* **2007**, *16*, 476−488. (c) Tobita, H. *Macromol. Symp.* **2008**, *261*, 36−45. (d) Tobita, H. *Macromol. Theory Simul.* **2009**, *18*, 108−119. (e) Tobita, H. *Macromol. Theory Simul.* **2009**, *18*, 120−126. (f) Tobita, H. *Macromol. Theory Simul.* **2010**, *288*, 16−24. (g) Tobita, H. *Macromol. Theory Simul.* **2011**, *20*, 179−190. (h) Tobita, H. *Macromol. Theory Simul.* **2011**, *20*, 709−720.

(9) Wakamatsu, J.; Kawasaki, M.; Zetterlund, P. B.; Okubo, M. *Macromol. Rapid Commun.* **2007**, *28*, 2346−2353.

(10) Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*; Academic Press: London, 1995.

(11) Ma, J. W.; Cunningham, M. F.; McAuley, K. B.; Keoshkerian, B.; Georges, M. K. *J. Polym. Sci.; Part A: Polym. Chem.* **2001**, *39*, 1081−1089.

(12) Sugihara, Y.; Zetterlund, P. B. Manuscript in preparation.

(13) (a) Prodpran, T.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. *Macromol. Symp.* **2000**, *155*, 1−14. (b) Pan, G.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M. S. *Macromolecules* **2001**, *34*, 481−488. (c) Keoshkerian, B.; MacLeod, P. J.; Georges, M. K. *Macromolecules* **2001**, *34*, 3594−3599. (d) Pan, G.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M. S. *Macromolecules* **2002**, *35*, 6915−6919. (e) Cunningham, M. F.; Tortosa, K.; Ma, J. W.; McAuley, K. B. *Macromol. Symp.* **2002**, *182*, 273−282. (f) Cunningham, M. F.; Xie, M.; McAuley, K. B.; Keoshkerian, B.; Georges, M. K. *Macromolecules* **2002**, *35*, 59−66. (g) Cunningham, M.; Lin, M.; Buragina, C.; Milton, S.; Ng, D.; Hsu, C. C.; Keoshkerian, B. *Polymer* **2005**, *46*, 1025−1032.

(14) (a) Asua, J. M. *Prog. Polym. Sci.* **2002**, *27*, 1283. (b) Landfester, K. *Macromol. Rapid Commun.* **2001**, *22*, 896.

(15) Maehata, H.; Buragina, C.; Cunningham, M.; Keoshkerian, B. *Macromolecules* **2007**, *40*, 7126−7131.

(16) Lin, M.; Hsu, J. C. C.; Cunningham, M. F. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5974−5986.