*Macromolecules* **2006,** *39,* 4256−4258

# Notes

## Particle Formation by Self-Assembly in Controlled Radical Emulsion Polymerizations

**Robert G. Gilbert***

*Key Centre for Polymer Colloids, School of Chemistry F11, Sydney University, Sydney NSW 2006, Australia*

*Received March 9, 2006*
*Revised Manuscript Received April 22, 2006*

### Introduction

Controlled ("living") radical polymerization (CRP)[1] can produce polymers of almost any desired molecular architecture. CRP in emulsion polymerization is best implemented using controlled-radical mediated self-assembly, which has been carried out for both nitroxide[2−4] and RAFT (reversible addition−fragmentation chain transfer)[5,6] mediated systems. This involves (i) controlled synthesis of a hydrophilic monomer (e.g., acrylic acid, AA) to a desired degree of polymerization (e.g., DP 5), (ii) further controlled polymerization with a hydrophobic monomer to another desired DP (e.g., 10), (iii) further controlled polymerization of these now surface-active diblocks, which then undergo self-assembly into particles, until the particle number density ($N_p$) becomes constant; and (iv) further controlled polymerization with whatever feed profile of monomers is desired. It is postulated that in step iii the diblocks at first freely migrate among the self-assembled entities (micellar or more complex structures[7] and newly formed particles); this migration is assumed to cease when chains become sufficiently long, at which stage $N_p$ becomes constant.[8] Irrespective of the nature of the self-assembled entities, the equilibrium state of assemblies of diblocks with sufficiently long hydrophobic components will be spherical latex particles. This Note derives a simple model to enable $N_p$, and hence particle size (by mass conservation[9]), to be readily predicted; $N_p$ and size are important determinants of latex properties.

### Model Development

A full description of particle formation and growth of CRP in disperse systems requires accounting for the lengths of all chains and radical compartmentalization within separate particles. The only way to implement this is through Monte Carlo modeling,[10] which uses extensive computational resources and does not lead to a simple means of presenting data. The present simpler treatment enables insights to be gained by showing the dependence of particle number and size on controllable parameters.

The treatment is in the spirit of Smith and Ewart,[11] who deduced an analytic form for $N_p$ in ordinary emulsion polymerizations by assuming inter alia that particle formation stops when the total surface area of growing particles adsorbs all surfactant. While the Smith−Ewart model has its limitations (many models, e.g.,[12] greatly refine their treatment), it provides a useful starting point. The present model has the same objective for emulsion polymerizations under controlled conditions. It ignores the distributions of both dormant and growing chains in a CRP and assumes *each* chain needs to grow to a critical DP $X_{crit}$ beyond which it cannot migrate; i.e., particle formation stops when

$$\bar{X}_n = X_{crit} \tag{1}$$

where $\bar{X}_n$ is the number-average degree of polymerization of (both dormant and growing) chains. In a CRP, chains are capped by an agent whose reversible cleavage results in a macroradical which can propagate; this agent can be a nitroxide, a dithioester, or a similar group (RAFT) or metal complex (ATRP).[1] The number of capped chains per particle is

$$n_{CAP} = \frac{A_s}{a_{CAP}} \tag{2}$$

where $A_s$ is the swollen area of a single particle and $a_{CAP}$ is the "headgroup" area of a capped chain. This latter will vary with initiator and with the number of hydrophilic monomer units. One has

$$A_s = \pi^{1/3}(6V_s)^{2/3} \tag{3}$$

where $V_s$ is the swollen volume of a single particle. By mass conservation and assuming volume additivity for monomer and polymer, one has[9]

$$V_s = \frac{\bar{X}_n n_{CAP} M_0}{d_P N_A} \frac{d_M}{d_M - [M]_p M_0} \tag{4}$$

where $d_P$ and $d_M$ are the density of polymer and monomer, $M_0$ is the monomer molecular weight, and $[M]_p$ is the monomer concentration in the particles. The second term in eq 4 is the contribution of monomer to swollen volume. Equations 2−4 yield

$$V_s = 36\pi\left(\frac{\bar{X}_n M_0}{a_{CAP} d_P N_A} \frac{d_M}{d_M - [M]_p M_0}\right)^3 \tag{5}$$

The growth rate is found by assuming that all particles grow at the same rate, i.e., ignoring compartmentalization effects except those arising from a value of the average number of radicals per particle, $\bar{n}$. The growth rate at time $t$ is then given by

$$\frac{d\bar{X}_n}{dt} = \frac{k_p[M]_p\bar{n}}{n_{CAP}} \tag{6}$$

The value of $\bar{n}$ for the small particles of significance in particle formation under controlled-radical conditions[13,14] is

---

* To whom correspondence should be addressed. Fax +61-2-9351 8651; Ph +61 2 9351 3366; e-mail gilbert@chem.usyd.edu.au.

10.1021/ma0605301 CCC: $33.50

governed by "zero−one" kinetics,[9,15] applicable to systems where entry of a radical into a particle already containing a growing radical results in rapid termination. In these systems, $\bar{n}$ is determined by the rate coefficients $\rho$ and $k$ for radical entry into, and exit from, latex particles and by the fates of both initiator-derived and exited radicals in the water phase; here "particles" includes both preexisting particles and entities such as micelles which have just been entered by a radical capable of propagating with monomer within this entity. There are reliable models for $\rho$ and $k$ in conventional emulsion polymerization with electrostatic stabilizers,[9,15−17] but in the present system, complications arise from the presence of (electro)steric stabilizer inherent in the self-assembly method[18] and from the kinetics of controlled-radical polymerization.

For this model, it is assumed that $\bar{n}$ is time-independent during the nucleation period. This admittedly crude approximation can be justified by noting that particle formation in the present self-assembly systems is significantly longer than the typical time scales of entry and exit events,[8] in which case a pseudo-steady state in $\bar{n}$ will be applicable. Note that $\bar{n}$ itself depends on $N_p$, as discussed later.

Development is now confined to RAFT systems, which require external initiator; extensions to self-initiated systems (e.g., nitroxides) are for the future. The "Maxwell−Morrison" model for $\rho$ in emulsion polymerization assumes that initiator-derived radicals propagate with monomer in the water phase and enter a particle only if they attain a critical degree of polymerization $z$ (or higher) such that they are surface-active; this process competes with water-phase termination. $N_p$ is found by assuming each $z$-mer, being surface-active, enters a micelle-like species (or whatever entity arises from association of the diblocks) and then forms a particle (rather than causing termination by entering a preexisting particle). Thence

$$N_p = 2k_d[I]\left\{\frac{\sqrt{2k_d[I]k_{t,w}}}{k_{p,w}[M]_w} + 1\right\}^{1-z} tN_A \qquad (7)$$

where $[M]_w$ is the monomer concentration in the water phase, $k_d$ is the initiator dissociation rate coefficient, [I] is the initiator concentration, $k_{t,w}$ and $k_{p,w}$ are water-phase termination and propagation rate coefficients, respectively (in these systems with low-solubility RAFT-capped diblocks, water-phase termination is probably by bimolecular termination rather than transfer to a RAFT agent), and $N_A$ is Avogadro's constant.

Solving eq 6 with time-independent $\bar{n}$ gives

$$\bar{X}_n{}^3 = \bar{X}_n{}^3{}_{|t=0} + Bt; \qquad B = \frac{k_p[M]_p\bar{n}a_{CAP}{}^3}{12\pi}\left(\frac{M_0}{d_P N_A}\,\frac{d_M}{d_M - [M]_p M_0}\right)^{-2} \qquad (8)$$

and thus

$$N_p = 2k_d[I]\left\{\frac{\sqrt{2k_d[I]k_{t,w}}}{k_{p,w}[M]_w} + 1\right\}^{1-z}\frac{X_{crit}{}^3 - X_n{}^3{}_{|t=0}}{B}N_A \qquad (9)$$

Equation 9 is the desired expression for particle number. The dependence on $\bar{n}$ (through $B$, eq 8), which depends on $N_p$, is taken into account by solving eq 9 iteratively, in conjunction with a model for $\bar{n}$ which incorporates the dependence on $N_p$.

## Sample Implementation

The system chosen for an illustrative calculation is RAFT-controlled self-assembly of styrene, with the data given by Sprong et al. at 80 °C.[8] The initial diblocks were targeted to produce 10 AA units and either 5 or 10 styrene units. For electrostatically stabilized latexes, the fate of exited radicals in this type of the zero−one system is to reenter another particle without aqueous-phase termination ("limit 2a"[9,19]); however, studies in the author's group have shown that for a small AA-stabilized latex exited radicals undergo termination before reentering ("limit 1"[9,19]). The steady-state $\bar{n}$ is then $= \rho/(2\rho + k)$. In this sterically stabilized system, $k$ was calculated from the model of Thickett and Gilbert;[18] this requires the particle size, which was assigned a constant average value, yielding $k = 4 \times 10^{-3}\ \mathrm{s}^{-1}$. The value for $\rho$ was calculated from the Maxwell−Morrison model (eq 20 of ref 16, which includes an explicit dependence on $N_p$) with $z = 2$ and the other parameter values given elsewhere for styrene,[20] except for $k_d = 6 \times 10^{-5}\ \mathrm{s}^{-1}$ (for V-501 initiator used in this system) and $k_p = 6.5 \times 10^2\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$,[21] as applicable at 80 °C. $N_p$ was then calculated using eq 9 (where $B$ depends on $\bar{n}$ and hence on $\rho$ and hence $N_p$) iteratively, starting with an initial guess for $N_p$ and continuing until convergence.

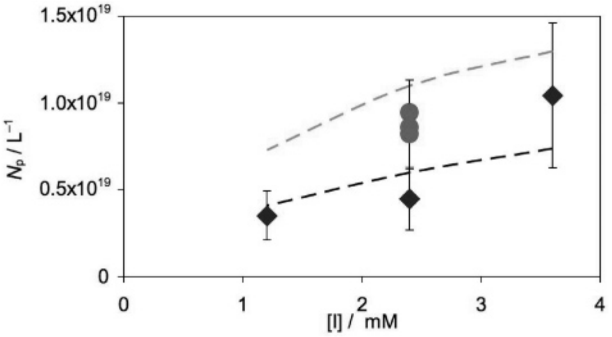

**Figure 1.** Points: dependence of $N_p$ on initiator concentration, as given by Sprong et al.[8] for RAFT-controlled self-assembly of diblocks desired to comprise initially 5 AA and 5 or 10 styrenes (circles and diamonds, respectively); thus, $\bar{X}_n{}^3{}_{|t=0} = 5$ and 10 in the model. Lines: calculated using the present model with parameters as described in the text.

Results are compared with experiment[8] in Figure 1; the values chosen for the other parameters were $a_{CAP} = 0.43\ \mathrm{nm}^2$ (chosen because this is the headgroup area of a typical ionic surfactant on a latex particle[22]) and $X_{crit} = 15$ (typical of the degree of polymerization when diblocks of this type migrate so slowly that they are suitable as stabilizers for miniemulsion polymerization[23]), both of which are physically reasonable. It is seen that accord with experiment is acceptable both for absolute values and for trends with initiator concentration and initial number of hydrophobic units in the diblock.

Equation 9 shows (through $B$) a strong dependence on $\bar{X}_n{}^3{}_{|t=0}$, $X_{crit}$, and $a_{CAP}$, although this sensitivity is tempered by the indirect dependence of $\bar{n}$ on these quantities (as seen in the relatively small change with $\bar{X}_n{}^3{}_{|t=0}$ in Figure 1). Equation 9 provides a starting point for design and optimization of controlled-radical self-assembly in emulsion polymerizations.

**Acknowledgment.** Discussions with Hank de Bruyn, Brian Hawkett, David Lamb, Joost Leswin, Ewan Sprong, and Stuart Thickett are gratefully acknowledged.

## References and Notes

(1) Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*, 2nd ed.; Elsevier: Amsterdam, 2006.
(2) Delaittre, G.; Nicolas, J.; Lefay, C.; Save, M.; Charleux, B. *Chem. Commun. (Cambridge, U.K.)* **2005**, 614−616.
(3) Nicolas, J.; Charleux, B.; Guerret, O.; Magnet, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 6186−6189.

(4) Nicolas, J.; Charleux, B.; Guerret, O.; Magnet, S. *Macromolecules* **2005**, *38*, 9963−9973.

(5) Ferguson, C. J.; Hughes, R. J.; Nguyen, D.; Pham, B. T. T.; Hawkett, B. S.; Gilbert, R. G.; Serelis, A. K.; Such, C. H. *Macromolecules* **2005**, *38*, 2191−2204.

(6) Ferguson, C. J.; Hughes, R. J.; Pham, B. T. T.; Hawkett, B. S.; Gilbert, R. G.; Serelis, A. K.; Such, C. H. *Macromolecules* **2002**, *35*, 9243−9245.

(7) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic: London, 1992.

(8) Sprong, E.; Leswin, J. S.; Lamb, D. J.; Ferguson, C. J.; Hawkett, B. S.; Pham, B. T.; Nguyen, D.; Such, C. H.; Serelis, A. K.; Gilbert, R. G. *Macromol. Symp.* **2006**, *231*, 84−93.

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

(10) Prescott, S. W. *Macromolecules* **2003**, *36*, 9608−9621.

(11) Smith, W. V.; Ewart, R. H. *J. Chem. Phys.* **1948**, *16*, 592−599.

(12) Coen, E. M.; Morrison, B. R.; Peach, S.; Gilbert, R. G. *Polymer* **2004**, *45*, 3595−3608.

(13) Prescott, S. W.; Ballard, M. J.; Gilbert, R. G. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **2005**, *43*, 1076−1089.

(14) Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Macromolecules* **2005**, *38*, 4901−4912.

(15) van Herk, A.; Gilbert, R. G. In *Chemistry and Technology of Emulsion Polymerisation*; Herk, A. v., Ed.; Blackwell Publishing: Oxford, 2005; p 328.

(16) Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1991**, *24*, 1629−1640.

(17) Morrison, B. R.; Casey, B. S.; Lacík, I.; Leslie, G. L.; Sangster, D. F.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 631−649.

(18) Thickett, S. C.; Gilbert, R. G. *Macromolecules* **2006**, *39*, 2081−2091.

(19) Casey, B. S.; Morrison, B. R.; Gilbert, R. G. *Prog. Polym. Sci.* **1993**, *18*, 1041−1096.

(20) van Berkel, K. Y.; Russell, G. T.; Gilbert, R. G. *Macromolecules* **2003**, *36*, 3921−3931.

(21) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.-D.; Manders, B. G.; O’Driscoll, K. F.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *196*, 3267.

(22) Ahmed, S. M.; El-Aasser, M. S.; Micale, F. J.; Poehlein, G. W.; Vanderhoff, J. W. In *Polymer Colloids II*; Fitch, R. M., Ed.; Plenum: New York, 1980; pp 265−287.

(23) Pham, B. T. T.; Nguyen, D.; Ferguson, C. J.; Hawkett, B. S.; Serelis, A. K.; Such, C. H. *Macromolecules* **2003**, *36*, 8907−8909.

MA0605301