Calculating Molecular Weight Distributions in Emulsion Polymerization under Conditions of Diffusion Limited Chain Transfer

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ABSTRACT: When highly reactive chain transfer agents with low water solubilities (e.g., long chain thiols) are used in emulsion polymerizations, transport of the chain transfer agent (CTA) from the monomer droplets to the polymer particles can become diffusion limited. Consequently, the concentration of CTA in the particles is lower than expected, resulting in apparent transfer constants that can be much lower than the actual transfer constants obtained from studies with homogeneous systems such as bulk or solution. Furthermore, molecular weights will be greater than those obtained in homogeneous systems with the same overall concentration of CTA. There are currently no techniques or methodologies available for predicting molecular weight distributions when the transport of CTA is diffusion limited. Apparent transfer constants may be used but they are typically restricted to a given system and operating conditions. In this work, we describe how the actual CTA concentration in the polymer particles can be estimated through analysis of instantaneous molecular weight distributions. This information is then used to calculate the cumulative molecular weight distribution during the polymerization. Comparisons with experimental molecular weight distributions validate the essential correctness of the approach, but also highlight potential problems. The extension of the approach to online applications is discussed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 217–227, 2000

Key words: emulsion polymerization; chain transfer; diffusion; molecular weight distribution

INTRODUCTION

Modifiers such as mercaptans are commonly added to emulsion polymerizations to regulate the molecular weight. In many cases, the water solubility of these chain transfer agents may be so low that their transport through the aqueous phase from the monomer droplets to the polymer particles becomes diffusion limited. This phenomenon has been recognized for many years.[1–5] For

example, in the production of styrene-butadiene rubber, high molecular weight mercaptans were deliberately chosen because they were effectively "self-metering" because of their low transport rates and thus were not consumed too rapidly in the early stages of polymerization.

It has been shown that for the aliphatic mercaptans used in emulsion polymerizations, dramatic changes in the effectiveness of chain transfer occur when the carbon number is varied.[6–14] Whereas the reactivity of radicals toward the mercaptan is only slightly sensitive to the carbon number, there are large differences in how the different size mercaptans partition between the monomer droplets, polymer particles, and the

aqueous phase. Transport rates between phases are also influenced by the carbon number. Lower molecular weight mercaptans have greater water solubility and therefore can migrate comparatively quickly between phases, whereas the extremely low water solubility of longer chain, high molecular weight mercaptans limits their transport rates. Further, it is possible for the radicals arising from chain transfer to diffuse out of the polymer particles if the carbon number is sufficiently low, thereby lowering the average number of radicals per particle and the polymerization rate.[15–19] Radicals arising from transfer to longer chain mercaptans, such as n-dodecanethiol (n-DDT), will generally not diffuse out of a particle because of their low aqueous phase solubility.

The role of the reactivity of monomer toward a given chain transfer agent is also an important consideration. Thiols are extremely reactive toward styrenic radicals but less reactive toward methacrylates and acrylates. For example, the transfer constant $C_{\mathrm{tr}} = k_{tr,A}/k_p$ is 15.6 for n-DDT in styrene but closer to unity for n-DDT and methyl methacrylate. Therefore, whereas some systems may be "self-metering" because of transport limitations, other systems may act in an analogous "self-metering" manner because of their inherent kinetic behavior.

In a homogeneous polymerization (e.g., solution or bulk), it is a straightforward procedure to estimate the molecular weight distribution of the polymer being produced at any instant, if the concentrations of chain transfer agent (CTA) and monomer are known. However, in an emulsion polymerization, the complexity of interphase mass transport makes predicting molecular weights more difficult. The CTA and monomer are partitioned between three phases: monomer droplets, aqueous phase, and particles. It is the concentrations of monomer and CTA in the particles that determine the molecular weight produced at any instant, but it is often very difficult or impossible to determine the CTA concentration inside the particles, $[A]_p$, during polymerization if mass transfer limitations exist. (The monomer concentration inside the particles can be calculated from thermodynamic relationships.) If the concentration of CTA in all the phases is at equilibrium, then $[A]_p$ can be calculated using available partitioning data. This is generally the case for CTAs with moderate solubility in water, including low molecular weight mercaptans, as well as CC_{l4} and CB_{r4}.

In many cases, however, the CTA concentrations in the different phases may not be at equilibrium and thus $[A]_p$ cannot be readily determined. Failure to achieve equilibrium usually results from a combination of low water solubilities (large partition coefficients) and high transfer constants, which result in the CTA being consumed in the polymer particles faster than it can diffuse from the monomer droplets to the polymer particles. The particles then become "starved" with respect to CTA. Without an accurate method to determine $[A]_p$ during polymerization, it is not possible to predict molecular weight, except perhaps using an empirically determined "apparent transfer constant." However, because transport rates depend on the total surface area (and hence diameter) of the monomer droplets and polymer particles,[12] apparent transfer constants usually change with any other factor influencing either the monomer droplet or polymer particle size distributions, including reactor scale, agitation, surfactant concentration, initiator concentration, and temperature.

Two approaches have been developed in recent years to calculate $[A]_p$ under diffusion limited conditions.[12,20] The first approach uses analyses of molecular weight data. Using deconvolution of instantaneous molecular weight distributions,[21–23] we have shown how $[A]_p$ can be calculated from experimental data.[20] The second approach uses a two film theory of mass transfer developed by Nomura et al.[12] They derived a mathematical model to predict consumption rates of CTA during reaction. However, their model can be adapted to allow calculation of $[A]_p$, provided monomer and CTA concentrations in the reactor could be obtained along with monomer droplet and polymer particle size distributions. Gas chromatography has traditionally been used to measure monomer and CTA concentrations, whereas newer laser diffraction particle sizers allow the simultaneous measurement of both the droplet and particle size distributions. The combination of these measurements with Nomura's model would allow simple calculation of $[A]_p$ during polymerization.

Using either of these two approaches, it may be possible to obtain accurate estimates of molecular weight distributions under conditions of diffusion limited chain transfer. It is the objective of this report to show how instantaneous and cumulative molecular weight distributions can be calculated from $[A]_p$ data when mass transfer limitations exist. Comparisons with experimental molecular

weight distributions are made, and potential weaknesses in the approach are discussed.

BACKGROUND

Determining $[A]_p$ by Molecular Weight Distribution Analysis

In our previous article,[20] a methodology was developed to determine the concentration of CTA concentration within the polymer particles, regardless of whether or not the CTA is at its equilibrium value. Seeded styrene emulsion polymerizations were run using n-DDT as the CTA. Because n-DDT has 12 carbon units and very low water solubility, n-DDT modified emulsion polymerizations are often subject to transport limitations. Through deconvolution of the raw gel permeation chromatography data, estimates of $[A]_p/[M]_p$ (the ratio of CTA concentration to monomer concentration in the particles) were made from analyses of pseudo-instantaneous number MWDs using kinetic models developed by Clay and Gilbert.[24] The seed particles were initially saturated with styrene and n-DDT, so that $[A]_p/[M]_p$ was at its equilibrium value at the beginning of the experiment. It was found that $[A]_p/[M]_p$ fell far below its equilibrium value soon after the polymerization was initiated and the system was unable to re-establish equilibrium during the remainder of the reaction. Values of $[A]_p/[M]_p$ were calculated to be very small, approximately 10^{-2}–10^{-3} of the equilibrium value. The following paragraphs briefly summarize those parts of the work required in the development of the current research.

The instantaneous number molecular weight distribution $P_{\text{inst}}(\text{MW})$ can be thought of as the MWD of the polymer that is formed over an infinitesimally small time interval. For a finite time interval Δt, $P_{\text{inst}}(\text{MW})$ is the difference between the cumulative number MWDs of two successive polymer samples, which have been sampled at times, t and $t + \Delta t$, i.e.:

$$P_{\text{inst}}(\text{MW}) = P_{\text{cum}}(\text{MW}, t + \Delta t) - P_{\text{cum}}(\text{MW}, t) \quad (1)$$

Instantaneous number MWDs collected over finite time intervals are more properly "pseudo-instantaneous" number MWDs.[21] From the pseudo-instantaneous number MWD, one can extract mechanistic information. Note that the contribution from the seed polymer must also be sub-

tracted so that only the molecular weight of the polymer made during the experiment is calculated.

Clay and Gilbert[24,25] have developed a model describing the instantaneous number MWD for both zero-one and pseudo-bulk emulsion polymerization systems. The instantaneous number MWD can be modeled by a single exponential for both zero-one and pseudo-bulk systems.

$$P_{\text{inst}}(\text{MW}) = \exp\left(\frac{k_{\text{tr},M}[M]_p + k_{\text{tr},A}[A]_p + \rho}{k_p[M]_p} \cdot \frac{\text{MW}}{M_0}\right)$$
$$\text{(zero-one)} \quad (2)$$

$$\lim_{\text{MW}\to\infty} P_{\text{inst}}(\text{MW})$$
$$= \exp\left(-\frac{k_{\text{tr},M}[M]_p + k_{\text{tr},A}[A]_p + (\langle k_t\rangle \bar{n}/N_A V_S)}{k_p[M]_p} \cdot \frac{\text{MW}}{M_0}\right)$$
$$\text{(pseudobulk)} \quad (3)$$

where MW is the polymer molecular weight, k_p is the propagation rate constant, k_{tr} is the transfer constant to monomer, $k_{\text{tr},A}$ is the transfer constant to chain transfer agent A, $[M]_p$ is the monomer concentration in the particles, $[A]_p$ is the CTA concentration in the particles, ρ is the entry rate coefficient, M_0 is the monomer molecular weight, $\langle k_t\rangle$ is an average termination rate constant, $\bar{n}$ is the average number of radicals per particle, N_A is Avogadro's number and V_S is the swollen particle volume.

If transfer is the dominant chain stopping event (i.e., $k_{\text{tr},A}[A]_p \gg \rho$, $k_{\text{tr},M}[M]_p$, $\leq k_t \geq \bar{n}/N_A V_S$), Eqs. (2) and (3) simplify to the following:

$$P_{\text{inst}}(\text{MW}) = \exp\left(-\frac{k_{\text{tr},A}[A]_p}{k_p[M]_p}\frac{\text{MW}}{M_0}\right) \quad (4)$$

Therefore, a plot of $\ln[P_{\text{inst}}(\text{MW})]$ versus MW should yield a straight line with a slope equal to $(-k_{\text{tr},A}[A]_p/k_p[M]_p M_0)$. Thus, from the instantaneous number MWDs, it is possible to determine $[A]_p/[M]_p$. Values for $k_{\text{tr},A}/k_p$ can be found for various monomer-chain transfer agent combinations in the literature. Using $k_{\text{tr},A}/k_p = 15.6$[26] for styrene/$n$-DDT, values for $[A]_p/[M]_p$ were calculated from the slopes of the linear regions of the instantaneous number distributions. Assuming $[M]_p$ is at equilibrium, the concentration of CTA inside the particles can then be determined. Christie and Gilbert[27] discuss application of this approach in their work.

Determining $[A]_p$ by Two Film Theory of Mass Transfer

Nomura et al.[12] developed a mass transfer model for emulsion polymerization that allows calculation of $[A]_p$ if the following measurements are available: monomer concentration in the reactor, CTA concentration in the reactor, monomer droplet size distribution, and polymer particle size distribution. As stated previously, all of these measurements can now be made either online or off-line with rapid response times. Their model, based on the two film theory of diffusion, accounts for transport of the CTA from the monomer droplets through the aqueous phase and into the polymer particles. It also accounts for consumption of the CTA by reaction inside the particles. Several individual diffusional steps are considered: diffusion through the bulk of the monomer droplet to the droplet surface, across the droplet–water interface into the aqueous phase, through the bulk of the aqueous phase to the particle surface, across the particle–water interface, and finally into the particle interior.

Their modeling was accompanied by experimental data using a series of mercaptans of various chain lengths (n-C7 to n-C12) in styrene emulsion polymerizations. They calculated that values of $[A]_p$ were often much lower than equilibrium concentrations ($\approx 10^{-1}$–10^{-3}), in close agreement with the values calculated in our work[20] using analysis of molecular weight distributions. Nomura's model was developed to enable prediction of the CTA consumption rate when diffusion limitations exist, which can be significantly lower than in the absence of diffusion limitations. No mention was made of using the model for molecular weight prediction; however, Nomura's model can provide the information required to predict the concentration of CTA within the particles, which in conjunction with the models developed by Clay and Gilbert, can be used to predict molecular weight distributions.

The Nomura model expresses the ratio of the actual CTA concentration in the particles to its theoretical equilibrium value as:

$$\frac{[A]_p}{[A]_{p,eq}} = \frac{1}{1 + \Omega} \qquad (5)$$

$$\Omega = \frac{(m/2\pi D_T)(1/d_d N_d + 1/d_p N_p)}{m/k_{tr}\bar{n}N_p m'} \qquad (6)$$

where $[A]_p$ is the actual CTA concentration in the particles, $[A]_{p,eq}$ is the equilibrium value, and Ω is a lumped term that represents diffusional resistance (m and m' are partition coefficients for droplets and particles respectively, D_T is the diffusion coefficient in the aqueous phase, d_d and d_p are the droplet and particle diameters respectively, N_d and N_p are the droplet and particle numbers respectively, k_{tr} is the chain transfer transfer parameter, and $\underline{n}$ is the average number of radicals per particle). Nomura et al.[12] reported that most of the diffusional resistance is from the diffusion across the droplet and particle interfaces, with smaller interfacial areas causing more diffusional resistance and therefore lowering $[A]_p$. Diffusion through the aqueous phase or through the bulk of the droplets and particles was found to be much faster than across the interfaces. The importance of the interfacial area in determining the CTA diffusion rate justifies the need to measure both droplet and particle size distributions.

Two procedures for determining $[A]_p$ have been described in this section. It will be shown in the following sections of this paper how $[A]_p$ estimates taken at various times during polymerization can be used to calculate instantaneous and cumulative molecular weights.

EXPERIMENTAL

Materials

Styrene (Aldrich, Milwaukee, WI) was washed three times each with a 2 wt % NaOH solution and distilled water, and then dried over $CaCl_2$ overnight, after which it was distilled under vacuum. The following chemicals were used as received: n-DDT (Aldrich), potassium persulfate (Fisher Scientific, Ottawa, Canada), sodium dodecyl sulfate (Fisher Scientific), sodium bicarbonate, hydroquinone, and Aerosol MA. Distilled, deionized water was used for all polymerizations.

Polymerizations

Polystyrene seed particles were prepared using an established procedure.[25] Before use, the seed latex was dialyzed using a Spectra/Por® Membrane. Table I summarizes the characteristics of the seed particles used in this study.

Experiments were conducted using 1 wt % and 5 wt % n-DDT (with respect to monomer). Control experiments were also run without n-DDT. Relatively high n-DDT concentrations were used to ensure the molecular weight varied significantly

Table I   Characteristics of Seed Polymers

Seed Latex	Unswollen Radius (nm)	$\bar{M}_n$ (Da)	$\bar{M}_w$ (Da)
Seed 6	67	137,960	461,170
Seed 7	58	149,360	456,730
Seed 8	64	137,360	460,290

during the polymerizations, thereby providing a more challenging case for molecular weight prediction. To obtain a wider range of kinetic conditions, runs were conducted for both zero-one and pseudo-bulk kinetics. (Styrene polymerizations are usually run under zero-one conditions.) Runs were classified as either zero-one or pseudo-bulk based on their behavior at the beginning of the experiment, using the criteria outlined in Gilbert.[25] Values of $\underline{n}$ were ≈ 4 for the pseudo-bulk runs and $0.48-0.50$ for the zero-one runs. The recipes for zero-one and pseudo-bulk seeded emulsion polymerizations are shown in Table II. Polymerizations were conducted in a 1-L glass reactor, maintained at 50°C using a circulating water bath and stirred at 400 rpm. The reactor was sparged with N_2 (BOC, 99.998% purity) to remove oxygen.

The reactor was charged with styrene, polymer seed, and n-DDT and then placed in a water bath at 50°C. The reactor contents were agitated overnight to saturate the polymer seed particles with styrene and n-DDT. An aqueous sodium lauryl sulfate and sodium bicarbonate solution was then added to the reactor and agitated. When the reactor temperature reached 50°C, the initiator solution was added to start the polymerization. Samples were withdrawn from the reactor periodically and short-stopped with a 2 wt % aqueous solution of hydroquinone and placed immediately in an ice bath. Monomer conversion was determined gravimetrically.

Analysis Of *n*-DDT Concentrations

The mass of n-DDT present within the polymer latex was determined using a Varian 3400 gas chromatograph (GC) equipped with a flame ionization detector. A known quantity of each latex sample was dissolved in tetrahydrofuran (THF) and injected directly into the GC. Ethylene glycol was used as the internal standard.

Molecular Weight Distributions

Molecular weight distributions were obtained using a Waters 2690 Separations Module equipped with a Waters 410 Differential Refractometer and Waters Styragel Columns. Data analysis was performed using the Millennium 2010 software package. A calibration curve was constructed from polystyrene standards spanning a molecular weight range of $8.7 \times 10^2 - 2.8 \times 10^6$ AMU (atomic mass units).

RESULTS AND DISCUSSION

Figure 1 shows the consumption of n-DDT as a function of monomer conversion for zero-one and pseudo-bulk runs. Under zero-one conditions, the n-DDT is consumed quickly. Under pseudo-bulk conditions, the n-DDT is not fully consumed until higher conversion ($>80\%$) is reached. Most of the modifying effect of the n-DDT on molecular weight is therefore limited to the early stages of reaction in the zero-one runs, and somewhat longer in the pseudo-bulk runs. The cause of these different behaviors is different mass transfer dynamics (and not inherent differences in the kinetics). Most diffusional resistance is due to limited surface area of the polymer particles and monomer droplets.[12] The zero-one and pseudo-bulk runs would have very different surface area profiles during the run, and would therefore experience different mass transfer limitations. With the zero-one runs, the particle number was higher than for the pseudo-bulk runs, giving higher interfacial areas for mass transfer and thereby allowing higher transport rates of the n-DDT into the particles. Further, a greater fraction of the n-DDT would be present in the particles at the start of the runs under zero-one conditions due to

Table II   Recipes Used in Zero-One and Pseudo-Bulk Seeded Emulsion Polymerization Experimsnts (*n*-DDT Weight Is with Respect to Styrene)

| System	Monomer (g)	SLS (g)	KPS (g)	DIW (g)	NaHCO$_3$ (g)	n-DDT (wt %)	N_c (dm^{-3})
01	245	0.83	2.0	575	1.0	0, 1, 5	8.0×10^{16}
PB	245	0.83	2.0	575	1.0	0, 1, 5	2.3×10^{15}
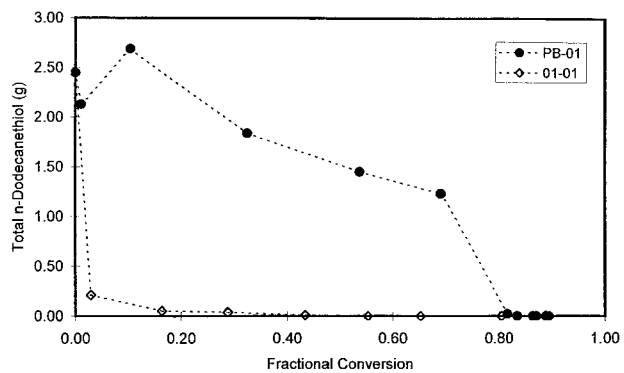
(a)
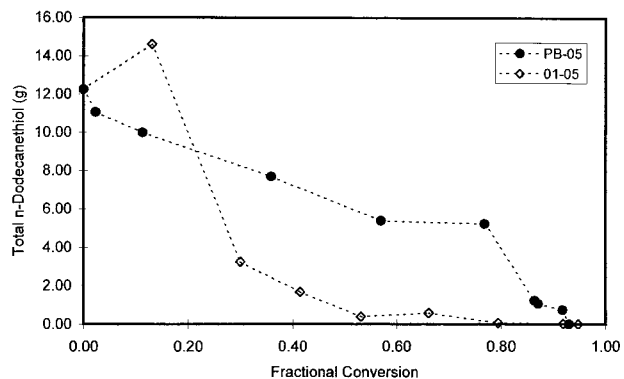
(b)

Figure 1 (a) Consumption profiles of n-DDT as a function of overall monomer conversion for runs with 1 wt % n-DDT. (b) Consumption profiles of n-DDT as a function of overall monomer conversion for runs with 5 wt % n-DDT.

the higher particle number. Therefore, more n-DDT would be available at the reaction site without having to diffuse from the monomer droplets in the zero-one runs.

Figure 2 illustrates three (cumulative) number molecular weight distributions at different conversions from a zero-one experiment with 1 wt % n-DDT. Taking the difference of two distributions yields the pseudo-instantaneous number molecular weight distributions.[21–23] From these pseudo-instantaneous distributions, $[A]_p$ was calculated as described earlier. The calculated value of $[A]_p$ represents an average over the given conversion interval. Smaller intervals (more frequent samples) will give more accurate measurements, provided the intervals are not so small that it becomes difficult to obtain accurate differential distributions. Instantaneous molecular weight distributions were calculated for all the experimental runs, and the values of $[A]_p$ were determined for each conversion interval.
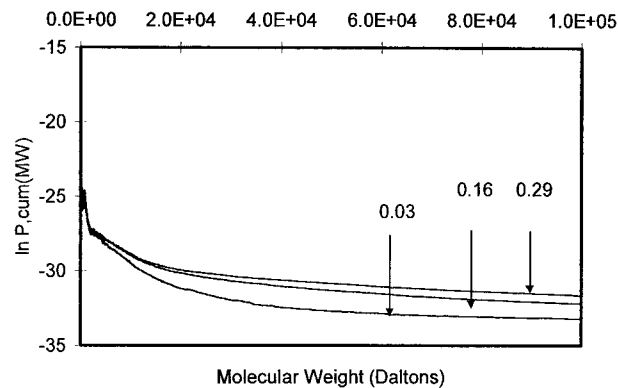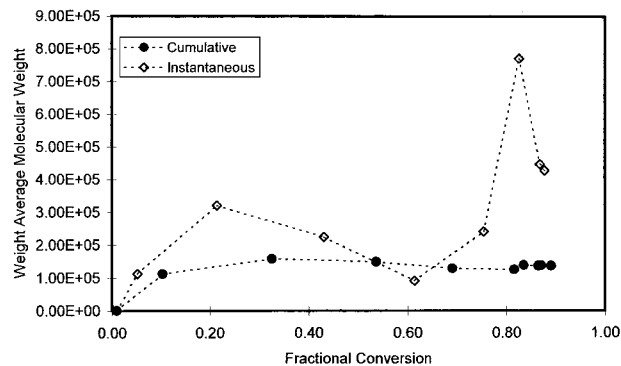

Figure 2 Cumulative number distributions for zero-one run with 1 wt % n-DDT.

The instantaneous weight average molecular weights are shown in Figures 3 and 4 along with the corresponding cumulative molecular weights. Because the instantaneous molecular weights
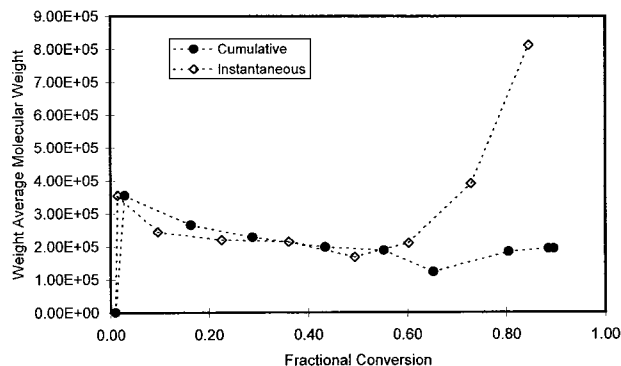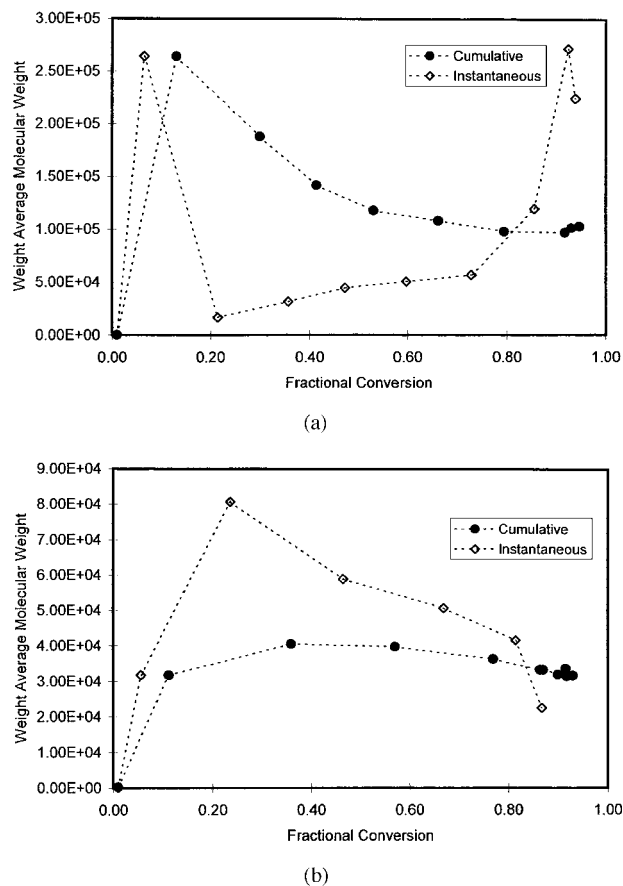

(a)

(b)

Figure 3 (a) Cumulative and pseudo-instantaneous molecular weight profiles for zero-one run with 1 wt % n-DDT. (b) Cumulative and pseudo-instantaneous molecular weight profiles for pseudo-bulk run with 1 wt % n-DDT.

(a)

(b)

Figure 4 (a) Cumulative and pseudo-instantaneous molecular weight profiles for zero-one run with 5 wt % n-DDT. (b) Cumulative and pseudo-instantaneous molecular weight profiles for pseudo-bulk run with 5 wt % n-DDT.

were calculated over finite conversion intervals, they represent average values over the interval. The number average molecular weights follow the same trends and thus are not shown. The molecular weights shown at 0% conversion are calculated values based on the known amounts of styrene and n-DDT initially present.

Despite having the same initial amount of n-DDT in the formulation, there are pronounced differences between the zero-one and pseudo-bulk runs, reflecting the differences in the consumption rates of n-DDT. In the zero-one experiment with 1% n-DDT [Fig. 3(a)], the instantaneous and cumulative molecular weight decreases up until about 50% conversion, after which it increases rapidly, coinciding with the disappearance of the n-DDT. Its gradual decrease early in the run indicates that that the n-DDT concentration in the particles continues to increase until ≈50% mono-

mer conversion. This behavior is quite different than what is observed in bulk or solution with styrene/n-DDT, where the molecular weight increases throughout the polymerization as then-DDT is consumed faster than monomer. With the higher n-DDT loading (5 wt %) under zero-one conditions [Fig. 4(a)], the downward drift in molecular weight is even more pronounced, and the instantaneous molecular weights are very low. The observed behavior seems to contradict the expected result, i.e., an increase in molecular weight as more n-DDT is consumed. However, calculations reveal the initial molecular weight produced in the particles should be very low (<5000) but by the time the first sample is taken the molecular weight has in fact already increased significantly as expected. However, the increase occurs over such a short conversion interval that the trend is not seen in the data, even though the first sample is taken at a few percent conversion. This extremely rapid consumption of n-DDT is consistent with its high transfer constant.

The pseudo-bulk runs [Fig. 3(b) and 4(b)] exhibit much different behavior, showing a slow increase in molecular weight near the start of the run followed by a decrease. The small decrease in molecular weight at the very end is the expected result of decreasing monomer concentration. (This is not always seen because it was not possible to obtain accurate number distributions at very high conversions.)

The increase in molecular weight at the start of the pseudo-bulk run is interesting. In the early parts of reaction, very low molecular weight polymer ($\overline{M}_n \approx 1300$ with 1% n-DDT) is produced because of the relatively high n-DDT concentration in the particles (recall they are initially saturated with n-DDT). However, the n-DDT is very rapidly consumed, resulting in a dramatic increase in molecular weight. (As an example of this effect, consider that in a bulk styrene polymerization, 80% of the n-DDT is consumed after 10% monomer conversion.) At this point, there is a significant driving force for diffusion of n-DDT from the droplets to the particles. This behavior is common to both the zero-one and pseudo-bulk runs. However, the initial diffusion rate of n-DDT from the droplets to particles is likely to be lower for the pseudo-bulk runs because of the small total particle surface area. (The particle number is lower for the pseudo-bulk runs.) If the diffusion rate is too low to replenish the rapidly reacting thiol, the thiol concentration in the particles remains low

and thus the molecular weight drifts upwards. As the run progresses and the particles grow, the transport rate of n-DDT from the droplets to the particles increases because of the increasing total particle surface area. The result is an increase in the thiol concentration within the particles and thereafter a decrease in molecular weight that continues until most of the n-DDT in the reactor has been consumed. With the 1 wt % n-DDT pseudo-bulk run, all of the n-DDT is eventually consumed, after which the molecular weight increases significantly. In the 5 wt % n-DDT run, there is still n-DDT remaining near the end of the reaction, and thus the molecular weight does not increase.

In the zero-one runs, we do not see the initial increase in molecular weight because the first sample is taken after most of the n-DDT initially present in the particles has already been consumed. Furthermore, the zero-one runs have a much higher particle number (and therefore initial surface area) than the pseudo-bulk runs, and therefore the initial transport rate is higher. Consequently, the replenishing of the particles with n-DDT and subsequent lowering of the molecular weight occurs faster.

It is perhaps more instructive to examine how the ratio $[A]_p/[A]_{p,\mathrm{eq}}$ (i.e., the actual n-DDT concentration in the particles divided by the concentration it would have if equilibrium existed) varies during the run. This ratio gives a measure of the extent of diffusional resistance. Higher ratios reflect low resistance, with a value of unity indicating no mass transfer limitations. Low ratios reflect greater diffusional resistance, with the particles becoming more "starved" of n-DDT as the ratio decreases. Figure 5 shows the ratio $[A]_p/[A]_{p,\mathrm{eq}}$ plotted versus monomer conversion. Its initial value is unity because the seed particles were saturated with n-DDT. If the n-DDT was not added until the start of reaction, the initial value would be zero. In calculating $[A]_p/[A]_{p,\mathrm{eq}}$, it was assumed that at equilibrium, the relative concentrations of n-DDT and styrene within the particle and droplet phases are equal,[12] i.e.: $[A]_d/[M]_d = [A]_p/[M]_p$ ($[A]_d$ and $[M]_d$ represent the concentrations of n-DDT and styrene in the droplet phase respectively). The actual value of the n-DDT concentration in the particles is determined as follows. Using GC measurements of the n-DDT concentration along with monomer conversion data and known thermodynamic data for styrene/polystyrene, $[A]_d/[M]_d$ was calculated using mass balance equations on n-DDT and styrene. Know-
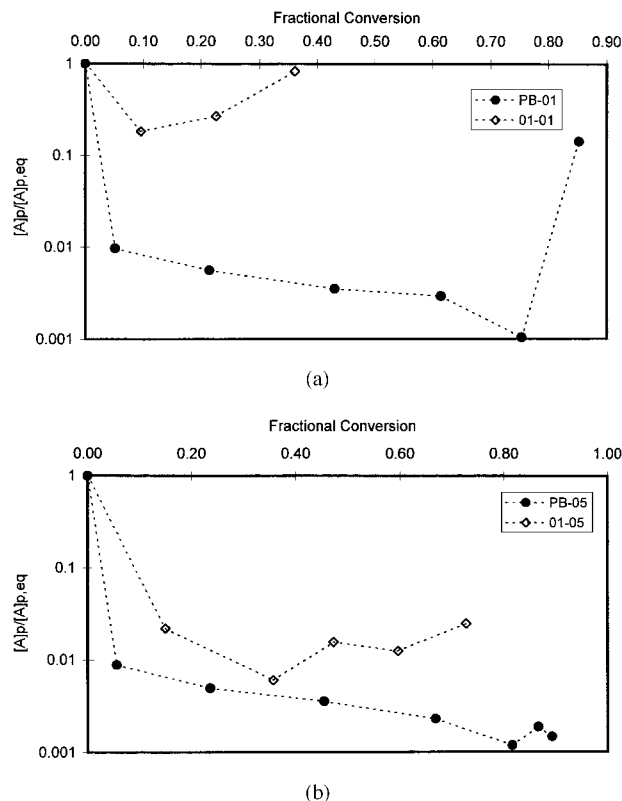
Figure 5   (a) $[A]_p/[A]_{p,\mathrm{eq}}$ versus monomer conversion for runs with 1 wt % n-DDT. (b) $[A]_p/[A]_{p,\mathrm{eq}}$ versus monomer conversion for runs with 5 wt % n-DDT.

ing the conversion, it can be readily determined whether monomer droplets exist using thermodynamic data. The amounts of monomer present in the droplets and particle phase respectively can then also be determined. The GC data for n-DDT and the instantaneous molecular weight distribution data together with Eq. (4) are then used to calculate how much n-DDT is present in each of the droplet and particle phases. In these calculations it was assumed that the concentrations of styrene and n-DDT in the aqueous phase was negligible.

$[A]_p/[A]_{p,\mathrm{eq}}$ rapidly decreases from unity for both zero-one and pseudo-bulk conditions. The observed values are on the order of 10^{-2} and 10^{-3} times less than its equilibrium value (unity). This departure from equilibrium is the result of the rapid consumption rates of n-DDT by reaction coupled with slow diffusion of n-DDT from the droplets to the particles. Because of the rapid consumption of n-DDT in the polymer particles (recall $C_{\mathrm{tr}} = 15.6$), $[A]_p/[M]_p$ drops significantly below its equilibrium value in a very short time. The rate of n-DDT diffusion is not fast enough to

keep up with its rate of consumption. This departure of $[A]_p/[M]_p$ from its equilibrium value has potentially severe consequences when attempting to predict the MWD of a polymer made by emulsion polymerization. To successfully model such a system, the dynamics of the partitioning behavior of the chain transfer agent between the droplet and particle phases must be quantitatively understood.

Calculating Cumulative Molecular Weight Distributions from $[A]_p$ Data

The preceding section examined how $[A]_p$ varies with reaction conditions and conversion. The following sections detail how cumulative molecular weight distributions can be determined once estimates of $[A]_p$ as a function of conversion are available. Many kinetic models for emulsion polymerization have been published, and although the form in which they are written may vary, their essence differs only slightly. In this work, we have chosen to use the instantaneous distributions shown in Eqs. (2) and (3). Typically the parameters shown in these equations will be known or can be easily calculated, with the exception of $[A]_p$ if diffusion limitations exist. Calculation of the molecular weight distribution for the pseudo-bulk case can be more complex than for the zero-one case because of the difficulty in estimating the average chain-length dependent termination rate coefficient, $\langle k_t \rangle$. However, when transfer to CTA is the dominant chain stopping mechanism, as it is in this work, there is negligible sensitivity to $\langle k_t \rangle$. Once values for $[A]_p$ and the kinetic parameters have been established, it is then a straightforward procedure to calculate the instantaneous number molecular weight distributions.

Instantaneous molecular weight distributions are valuable because of the mechanistic insight they can provide, but it is the cumulative molecular weight distribution or cumulative molecular weight averages that are usually the product specification. We therefore need to convert the instantaneous number distributions at given conversions to cumulative number distributions. This is done by integrating the instantaneous distributions over each conversion interval.

$$P_{\text{cum}}(\text{MW},x) = \int_{xi}^{xf} P_{\text{inst}}(\text{MW},x')dx' \qquad (7)$$

When the cumulative number distributions have been obtained, it may prove useful to convert them to cumulative weight distributions, as this is the more commonly used form.

$$X(\text{MW}) = \text{MW}^2 \cdot P_{\text{cum}}(\text{MW}) \qquad (8)$$

We will consider two methods that could be used to construct cumulative molecular weight distributions. The first uses our estimates of $[A]_p$ obtained from instantaneous molecular weight distributions. This procedure is therefore a test of the effectiveness of using relatively few data points based on pseudo-instantaneous molecular weight distributions[21] together with a theoretical kinetic model to calculate $[A]_p$, and then using that information to estimate the cumulative molecular weight distribution throughout the polymerization. The ability of the procedure to accurately reproduce the experimental molecular weight distribution would validate the idea of using pseudo-instantaneous molecular weight distributions with Gilbert's model equations in estimating $[A]_p$. Our case is particularly challenging because of the large changes in instantaneous molecular weight during reaction.

Figures 6 and 7 show calculated and experimental cumulative molecular weight distributions at different conversions for zero-one and pseudo-bulk runs with 1% n-DDT. In general, the technique developed in this work closely approximates the actual distribution, although the Figures illustrate two discrepancies observed in most of the molecular weight distributions. The calculated distributions tend to be slightly narrower than the observed distributions. The pseudo-bulk runs in particular show a greater fraction of high molecular weight polymer than the calculated distribution. This may be due to some bimolecular termination between two long macro-radicals, or it may simply be caused by GPC peak broadening. Broader experimental distributions may also result from significant molecular drift during the sampling intervals. This is more of an issue in the early stages of polymerization when the n-DDT concentration in the particles changes rapidly. Unfortunately, it is also difficult to avoid because of the exceptionally high reactivity of n-DDT toward styrenic radicals, which can cause substantial molecular drift over even very small conversion intervals. The n-DDT/styrene system has an exceptionally high transfer constant. Most systems have a much lower transfer constant and hence this problem will usually be less severe.
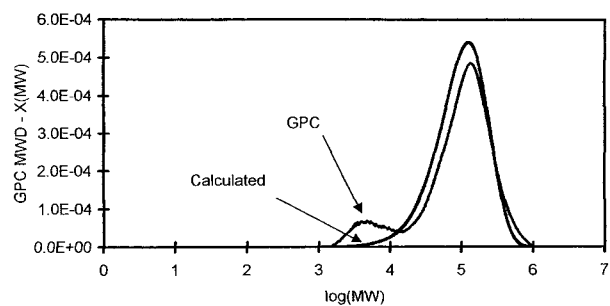
The second discrepancy is the poor prediction of very low molecular weight polymer that is com-
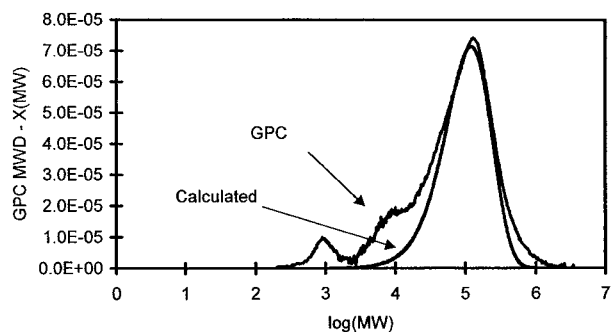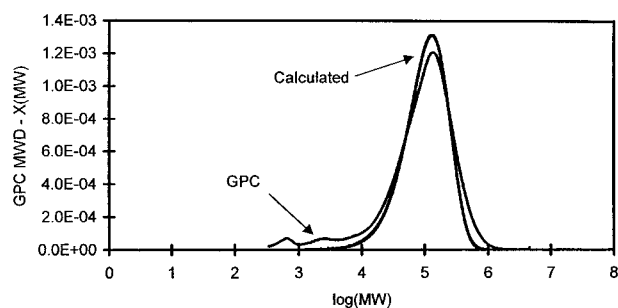
(a)
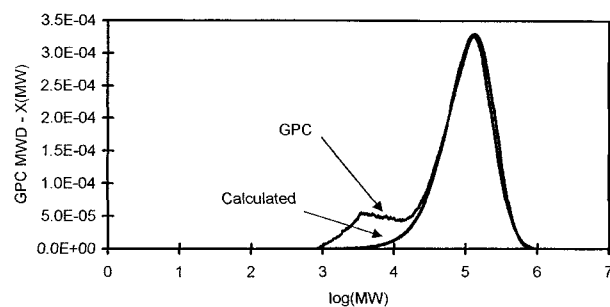
(b)

(c)

Figure 6 (a) Comparison of experimental and calculated molecular weight distributions for zero-one run with 1 wt % n-DDT (16% conversion). (b) Comparison of experimental and calculated molecular weight distributions for zero-one run with 1 wt % n-DDT (55% conversion). (c) Comparison of experimental and calculated molecular weight distributions for zero-one run with 1 wt % n-DDT (89% conversion).

prevent the very low molecular weight polymer from being made. If the n-DDT was not added until after initiation, the particles would initially contain no n-DDT. This is probably a more desirable procedure industrially because it prevents formation of very low molecular weight polymer.

The second method to calculate cumulative molecular weight distributions would use Nomura's model to calculate $[A]p$ but would then be identical to the procedure described above. The ap-

(a)
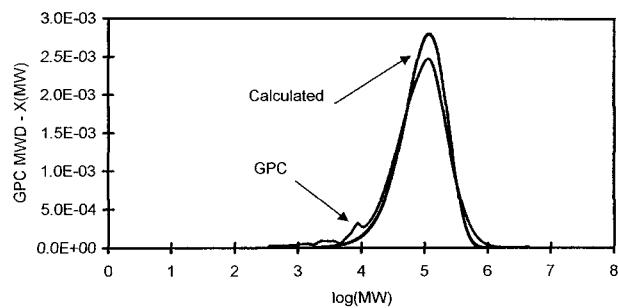
(b)
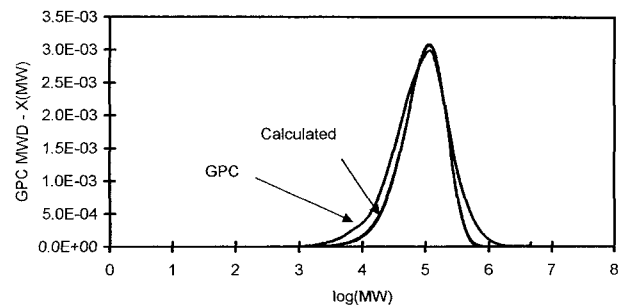
(c)

Figure 7 (a) Comparison of experimental and calculated molecular weight distributions for pseudo-bulk run with 1 wt % n-DDT (33% conversion). (b) Comparison of experimental and calculated molecular weight distributions for pseudo-bulk run with 1 wt % n-DDT (69% conversion). (c) Comparison of experimental and calculated molecular weight distributions for pseudo-bulk run with 1 wt % n-DDT (89% conversion).

monly observed. This low molecular weight polymer is produced in the initial stages of reaction when the particles were initially saturated with n-DDT. The failure to predict this tail can be attributed to insufficient data at low conversions when $[A]_p$ is dropping rapidly, and again highlights the need for frequent sampling at times in the reaction when $[A]_p$ may be changing quickly. Alternatively, the process could be modified to

proach based on molecular weight distribution analysis is a more rigorous technique appropriate for analyzing mass transfer phenomena; however, this technique is not adaptable for online use. Using Nomura's model would have the advantage of potential online application, because it requires only gas chromatography measurements of the monomer and CTA, and the droplet and particle size distributions. This approach is currently being developed in our laboratory and will be the subject of a future manuscript.

CONCLUSIONS

Chain transfer in emulsion polymerization has been studied under conditions in which the transport of the chain transfer agent from the droplets to the particles is diffusion limited. The concentration of CTA in the polymer particles can be significantly below its equilibrium value, as was observed for styrene polymerizations using n-DDT. Using values of $[A]_p$ calculated from experimental data, we have shown that molecular weight distributions can be accurately calculated, even when particles are severely starved of n-DDT. More frequent sampling would improve the accuracy further. Previously it has not been possible to calculate molecular weights when transport of the CTA is diffusionally limited, except perhaps using empirical approaches. The methodology used herein may be amenable to online application using the mass transfer model developed by Nomura et al.[12]

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