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Measuring the Effectiveness of n-Dodecanethiol as a Chain Transfer Agent in Styrene Emulsion Polymerization

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SUMMARY: A method was developed to determine the concentration of chain transfer agent inside polymer particles during reaction using instantaneous molecular weight distributions. For highly active chain transfer agents with low water solubility, the chain transfer reaction may be diffusion limited. This methodology provides insight into whether diffusion limitations exist. Data for the system styrene/n-dodecanethiol quantitatively demonstrates the extent of the diffusion limitation in the chain transfer reaction.

Introduction

Chain transfer agents (CTAs) are widely used to regulate molecular weight in emulsion polymerizations. Typically the CTA and monomer are consumed at different rates, resulting in either upward or downward drift in the average molecular weight. If the transfer constant C_{tr} (k_{tr}/k_p)>1, CTA is consumed faster than monomer, while if $C_{tr}<1$, monomer is consumed faster than the CTA. In a homogeneous polymerization, it is a straightforward procedure to estimate the molecular weight distribution being produced at any instant during a polymerization if the concentrations of chain transfer agent and monomer are known. However in an emulsion polymerization, the role of chain transfer agents is more complex.1-8) The CTA and monomer are partitioned between three phases: monomer droplets, aqueous phase, and particles. It is the concentrations in the particles that determines 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 a process. (The monomer concentration inside the particles can be calculated from thermodynamic relationships.) If the CTA is in equilibrium between all phases, then $[A]_p$ can be calculated. In many cases, however, the CTA may not be at equilibrium and thus $[A]_p$ cannot be readily determined.3) Failure to achieve equilibrium could result from very low water solubilities (large partition coefficients) of the

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CTA and/or high transfer constants, which result in the CTA being consumed by reaction faster than it can diffuse from the monomer droplets to the polymer particles. The particles are then "starved" with respect to CTA. Without an accurate method to determine $[A]_p$ during reaction, it is not possible to predict the molecular weight being produced. It is the objective of this work to develop a methodology to determine the CTA concentration within the particles during reaction and study how the instantaneous MWDs are affected.

Experimental

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

Polymerizations. Polystyrene seed particles were prepared using an established procedure.$^{9)}$ Before use, the seed latex was dialyzed using a Spectra/Por ® Membrane. Table 1 summarizes the characteristics of the seed particles used in this study.

Table 1 - Characteristics of seed polymers.

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

Experiments were conducted using 1 wt% and 5 wt% n-DDT (with respect to monomer). Control experiments were also run without n-DDT. Only the 1 wt% runs will be discussed in this paper. To obtain a wider range of kinetic conditions, runs were conducted for both zero-one and pseudobulk kinetics. (Styrene polymerizations are usually run under zero-one conditions.) Runs were classified as either zero-one or pseudobulk based on their behaviour at the beginning of the experiment, using the criteria outlined in Gilbert.$^{9)}$ Values of $\bar{n}$ were ~4 for the pseudobulk runs and 0.48-0.50 for the zero-one runs. The recipes for zero-one and pseudobulk seeded emulsion polymerizations are outlined in Table 2.

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 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, initiator solution was added to start polymerization. Samples were taken periodically and short-stopped with a 2 wt% aqueous solution of hydroquinone and placed immediately in an ice bath. Monomer conversion was determined by gravimetry.

Table 2 - Recipes used in zero-one and pseudobulk seeded emulsion polymerization experiments. (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}

Analysis of n-dodecanethiol concentrations The mass of n-dodecanethiol was measured by gas chromatography (GC). A Varian 3400 gas chromatograph equipped with a flame ionization detector was employed for this analysis. A known quantity of each latex sample was dissolved in THF and injected 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. A calibration curve was constructed from polystyrene standards spanning a range of 8.7×10^2-2.8×10^6 Da.

Results and Discussion

The cumulative number molecular weight distribution $P_{cum}(MW)$ is a record of all the dead polymer chains formed during polymerization. However it is often more useful to consider the *instantaneous* number MWD, $P_{inst}(MW)$. $P_{inst}(MW)$ can be thought of as the MWD of the polymer that is formed over an infinitesimally small time interval. $P_{inst}(MW)$ 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.:

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

Ideally, Δt should be infinitesimally small. However, for very small conversion intervals, it is difficult to accurately determine small differences in MWDs.[13)] For these reasons, it is necessary to collect polymer samples over larger periods of time. Instantaneous number MWDs collected over these larger conversion intervals should then properly be considered as "pseudo-instantaneous" number MWDs. The theory behind this deconvolution technique and its practical applications are discussed in references 11 and 13.

Clay and Gilbert[10)] and Miller et al.[12)] have developed a model describing the instantaneous number MWD for both zero-one and pseudobulk emulsion polymerizations. The model predicts that the instantaneous number MWD can be modeled by a single exponential for both zero-one and pseudobulk systems.

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

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

where, $k_{tr,M}$ and $k_{tr,A}$ are the chain transfer rate coefficients for transfer to monomer and chain transfer agent respectively, $[M]_p$ and $[A]_p$ are the concentrations of monomer and chain transfer agent in the particle phase respectively, ρ is the pseudo-first-order entry rate coefficient per polymer particle, k_p is the propagation rate coefficient, MW and M_0 are the molecular weights of the polymer and monomer respectively, $\langle k_t\rangle$ is the average chain-length dependent termination rate coefficient, $\bar{n}$ is the average number of free radicals per polymer particle, N_A is Avagadro's number and V_S is the swollen latex particle volume.

When significant concentrations of chain transfer agent exist, chain transfer will be the dominant chain stopping event (i.e. $k_{tr,A}[A]_p \rangle\rangle \rho, k_{tr,M}[M]_p, \langle k_t\rangle \bar{n}/N_A V_S$). Under these conditions, Equations 2 & 3 simplify to:

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

Therefore, a plot of $P_{inst}(MW)$ versus MW should yield a straight line with a slope equal to $-k_{tr,A}[A]_p/k_p[M]_p M_0$. From the instantaneous number MWDs, it is thus possible to determine $[A]_p/[M]_p$, given $k_{tr,A}/k_p$. (The procedure must be modified when conducting seeded polymerizations to properly account for the presence of the seed polymer and ensure it is the MWD of the newly formed polymer that is being calculated.) Using $k_{tr,A}/k_p$ = 15.6^17) for styrene/n-DDT, values for $[A]_p/[M]_p$ were estimated from the slopes of the linear regions of the instantaneous number distributions. This technique has also been used by other researchers to obtain estimates for $k_{tr,M}$ and $k_{tr,A}$.^12,15,16) Assuming $[M]_p$ is at equilibrium, the concentration of CTA inside the particles is then easily calculated.

Figure 1 shows the measured n-DDT mass as a function of conversion for zero-one and pseudobulk runs with 1wt% n-DDT. Under zero-one conditions, the n-DDT is consumed quickly, and is essentially fully reacted after ~50% conversion. Under pseudobulk conditions, the n-DDT is not fully consumed until ~80% conversion. The modifying effect of the n-DDT on molecular weight is limited to the first half of reaction in the zero-one case, while it extends for most of the reaction in the pseudobulk experiments. The probable cause of these different behaviors is different mass transfer dynamics (and *not* inherent differences in the kinetics). Nomura^3) has shown that most diffusional resistance is due to limited surface area of the polymer particles and monomer droplets. The zero-one and pseudobulk runs would have very different surface area profiles during the run, and would therefore experience different mass transfer limitations. These issues will be further explored in a forthcoming paper.

It is known that KPS can react with n-DDT. This reaction would have to be considered if one were attempting to predict n-DDT consumption. However it does not affect the method here as we rely on measurements of n-DDT From the pseudo-instantaneous MWDs, the instantaneous weight average MWs, $\overline{Mw}_{inst}$, were calculated (Figures 2 and 3). In the zero-one experiment (Figure 3), the instantaneous molecular weight drifts downward up to about 50% conversion, after which it increases rapidly, coinciding with the disappearance of the n-DDT. The pseudobulk run (Figure 2) follows a similar trend, except that it shows a small increase near the start of the run and a decrease near the end of the run. The decrease at the end is the expected result of decreasing monomer

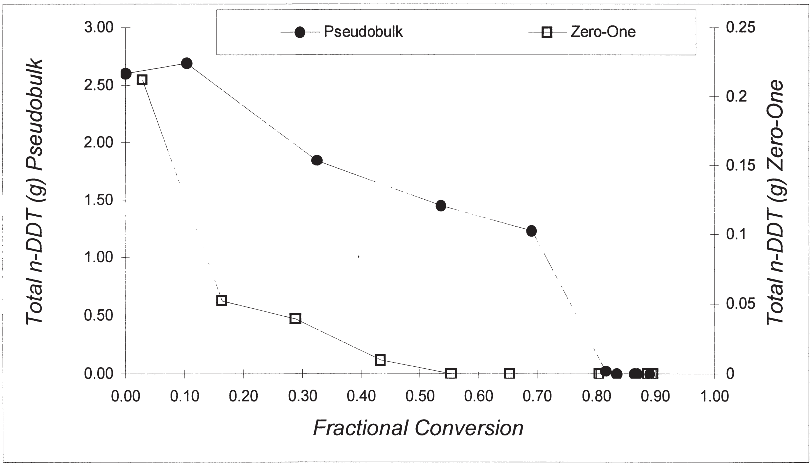

Figure 1. Measured n-DDT in reactor versus conversion (1 wt% n-DDT)

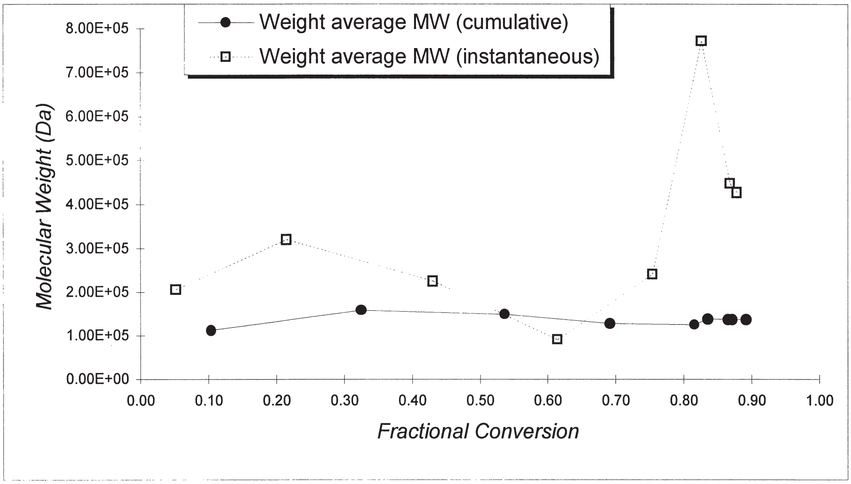

Figure 2. Molecular weight as a function of conversion for pseudobulk run.

concentration, although it may also be due to small errors in GPC measurements over short conversion intervals. The increase in molecular weight at the start of the pseudobulk run is interesting behavior. In the early parts of reaction, very low molecular weight polymer is produced because of the relatively high n-DDT concentration in the particles (recall they are initially saturated with n-DDT). The initial diffusion rate of n-DDT from the droplets to particles is probably low because of the small particle surface area (small Nc). If the diffusion rate is too low to replenish the rapidly reacting thiol, the thiol concentration in the particles decreases and thus the molecular weight drift upwards. As the run progresses, the transport rate of n-DDT from the droplets to the particles increases as the particle surface area increases. The result is an increase in the thiol concentration within the particles and therefore a decrease in molecular weight that continues until most of the n-DDT in the reactor has been consumed, at which time the molecular weight begins rising. The zero-one runs do not show an initial increase in molecular weight. They have a much higher particle number (and therefore surface area) than the pseudobulk runs; mass transfer rates are therefore always greater than for pseudobulk.

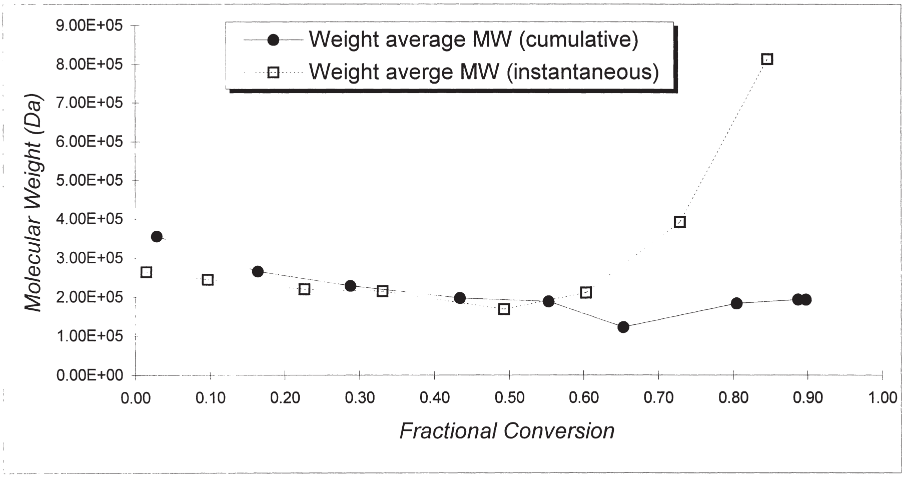

Figure 3. Molecular weight as a function of conversion for zero-one run.

Nomura[3)] reported that at equilibrium, the relative concentrations of n-DDT and styrene within the particle and droplet phases are equal, i.e.: $\frac{[A]_d}{[M]_d} = \frac{[A]_p}{[M]_p}$ (5)

Here, $[A]_d$ and $[M]_d$ represent the concentrations of n-DDT and styrene in the droplet phase respectively. Prior to initiation, the polymer seed particles were saturated with styrene and n-

DDT and therefore at equilibrium. Using GC measurements of the n-DDT concentration along with conversion data, $[A]_d/[M]_d$ was estimated using mass balance equations on n-DDT and styrene. It was assumed that the concentrations of styrene and n-DDT in the aqueous phase were negligible. The theoretical equilibrium ratio ($[A]_p/[M]_p:[A]_d/[M]_d$) was then calculated for each conversion interval. At equilibrium, the ratio of $[A]_p/[M]_p:[A]_d/[M]_d$ is 1.

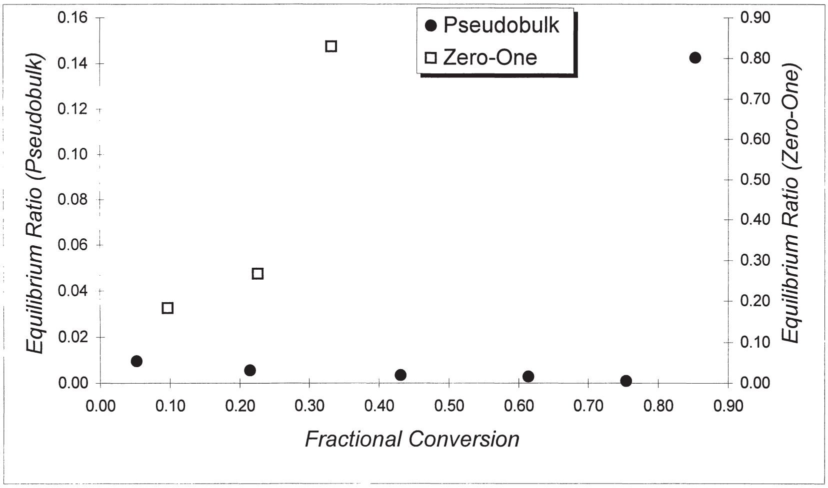

Figure 4. Equilibrium ratio versus conversion for zero-one and pseudobulk runs.

However analysis of the data revealed that its actual values are on the order of 10^{-2} and 10^{-3} times less than its equilibrium value predicted by Equation 5. Figure 4 shows the ratio $[A]_p/[M]_p:[A]_d/[M]_d$ plotted versus conversion. Its initial value is unity (seed particles were saturated with n-DDT), but it rapidly decreases for both zero-one and pseudobulk conditions. It is believed that this large departure from equilibrium was the result of the rapid consumption rates of n-DDT by reaction coupled with slow diffusion of n-DDT through the aqueous phase. Due to the rapid consumption of n-DDT in the polymer particles particle (recall C_{tr}=15.6), $[A]_p/[M]_p$ quickly dropped significantly below its equilibrium value. The rate of n-DDT diffusion was apparently not fast enough to keep up with its rate of consumption. It is an interesting historical note that this phenomenon was first reported many years ago, and in fact is desirable in some systems where the CTA is essentially self-metering.$^{18)}$

Conclusions

The seeded emulsion polymerization of styrene was investigated to study the effects of n-dodecanethiol on the polymer molecular weight distribution. A methodology has been developed to allow determination of the CTA concentration within the particles, regardless of whether or not the CTA is at its equilibrium value. $[A]_p/[M]_p$ fell far below equilibrium values soon after initiation and was unable to re-establish equilibrium during reaction. This is likely due to the slow rate of n-DDT diffusion through the aqueous phase and the highly reactive nature of n-DDT. Values for $[A]_p/[M]_p/[A]_d/[M]_d$ were estimated to be approximately 10^2-10^3 times less than the equilibrium value.

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