Kinetics of Dispersion Polymerization of Methyl Methacrylate and *n*-Butyl Acrylate: Effect of Initiator Concentration

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ABSTRACT: The effects of initiator concentration on the kinetics of methyl methacrylate (MMA) and *n*-butyl acrylate (*n*-BuA) dispersion polymerizations were studied by reaction calorimetry. It was found that increasing the initiator concentration increased the reaction rate as well as the particle size in both systems. Three stages were distinguished in the reaction rate profiles of both MMA and *n*-BuA dispersion polymerizations. However, the dependencies of the reaction rate (initial and maximum R_p) on initiator concentration differed significantly for the two systems. This was interpreted on the basis of partitioning of monomer and initiator between phases, resulting in shifts in the reaction loci with conversion as indicated by the evolution of the molecular weight distributions.

Introduction

Dispersion polymerization has gained a lot of attention due to its simplicity in producing micron-size polymer particles (1−10 μm) with narrow particle size distributions, which have a wide variety of applications in areas such as column packing materials for chromatography, biomedical diagnostics, protein recovery, drug delivery, and coatings.[1] To prepare polymer particles in this size range with a narrow size distribution, various techniques have been developed on the basis of emulsion polymerization utilizing seeded processes. For example, an activated swelling process[2] was developed by Ugelstad and patented in 1984.[3] Another technique, seeded emulsion polymerization,[4] has the ability to prepare polymer particles as large as 100 μm with narrow particle size distributions. However, these processes are complex and can be difficult to reproduce. A high degree of swelling or a larger number of seeding steps are necessary to enlarge the seed particles.

Dispersion polymerization has the advantage of making micron-size polymer particles in one single polymerization step. However, one of the difficulties of utilizing dispersion polymerization in practice is that the kinetics and mechanism are poorly understood, which makes control of particle properties in terms of size and size distribution rather empirical.

Methyl methacrylate (MMA) and *n*-butyl acrylate (*n*-BuA) were chosen for this study since the dependencies of the particle size on initiator concentration were reported to be of the opposite sign for these two systems.[5,6] In MMA dispersion polymerization in methanol, it was found that the particle size increases with increasing initiator concentration while in *n*-BuA dispersion polymerization in methanol/water (90/10 w/w), the reverse trend was found. The former results at first may appear counterintuitive; however, several explanations have been proposed for this phenomenon. All but one of them attribute fewer particles to fewer chains being able to grow to a sufficient length either to become nuclei or to act to stabilize particles (grafted stabilizer); this is based on increased termination with increasing initiator concentration.[7] A different mechanism was proposed by Tseng et al.[8] It was suggested that two factors are crucial in determining the number of mature particles: one is the nucleation rate, and the other is the adsorption rate of stabilizer on the unstable nuclei. A greater aggregation rate results from a higher initiator concentration, which leads to fewer mature particles forming, and thus producing a larger particle size. A faster adsorption rate of the stabilizer tends to result in smaller particles. It is believed that the balance of these differs for various systems, and consequently, the effect of initiator concentration on particle size differs for MMA (or St) and *n*-BuA.[9]

This paper describes systematic kinetics studies of the dispersion polymerization of MMA and *n*-BuA using a reaction calorimeter and concentrates on the study of the effect of initiator concentration. Other papers will report on the effects of stabilizer and medium composition in these two systems.

Experimental Section

Materials. The monomers, *n*-butyl acrylate (*n*-BuA) and methyl methacrylate (MMA) (Fisher Scientific), were purified via vacuum distillation. 2,2′-Azobis(isobutyronitrile) (AIBN, Sigma-Aldrich) was used as initiator without further purification. All other materials were used without further purification, including methanol and toluene (VWR) and poly(vinylpyrrolidone) (PVP K-30) (Sigma-Aldrich). Deionized (DI) water was used in all experiments. The standard recipe used for the kinetics studies of MMA and *n*-BuA dispersion polymerizations is shown in Table 1. The final polymer solids content at complete conversion is ∼10 wt %.

Polymerization Using the Reaction Calorimeter (RC1). Kinetics studies were carried out in a 1 L reactor (MP10) using the Mettler RC1 reaction calorimeter. All ingredients were initially charged into the reactor except the initiator solution. The reactor was purged with nitrogen for about 15 min and checked for leaks. Calibration was performed to determine the heat transfer coefficients and heat capacities required to calculate the heat of reaction with time ($Q_r(t)$) from the reactor and jacket fluid temperature data. It was then sealed, followed by ramping the temperature to the specified reaction temperature over 10 min. An initiator solution (6 mL) was then injected after a stable reaction temperature was reached. During the whole reaction, the temperatures were recorded by the RC1 for later calculation of $Q_r(t)$. Samples (about 2 mL) were periodically withdrawn via syringe from the reactor for particle size analysis and quenched by addition of a drop of 1% aqueous hydroquinone solution and by cooling in an ice bath. The fractional conversion obtained via RC1 calorimetry was scaled by the gravimetric final conversion.

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Table 1. Recipe for Dispersion Polymerizations of MMA Using the RC1 (70 °C, 400 rpm)

ingredient	weight (g)	percent[a] (%)
MMA or *n*-BuA	50.54	100
AIBN[b]	varied	varied
PVP K-30[c]	10.1072	20
methanol/water (70/30 w/w)	449.38	

[a] Based on monomer. [b] 2,2′-Azobis(isobutyronitrile). [c] Poly(vinylpyrrolidone) PVP K-30, MW = 40 000 g/mol.

Table 2. Particle Size as a Function of Initiator Concentration in MMA and *n*-BuA Dispersion Polymerizations

	particle diameter (μm)	
[AIBN] (mM)	MMA	*n*-BuA
2.5	2.65	1.08
5.0	3.14	1.25
7.5	4.80[a]	1.28
10.0	6.10[a]	1.60

[a] Polydisperse.

The reaction rate (R_p) was calculated from the heat of reaction (Q_r) evaluated by the RC1:

$$R_p = \frac{Q_r}{(-\Delta H)V} \tag{1}$$

where R_p is the reaction rate (mol/L/s), Q_r is the rate of heat generation by the reaction (kJ/s), $-\Delta H$ is the molar heat of polymerization of the monomer (kJ/mol), and V is the total volume of the system. The molar heats of polymerization of MMA and *n*-BuA are reported to be −57.8 and −78 kJ/mol, respectively.[10]

Latex Characterization. Scanning electron microscopy (SEM, Jeol 6300F) was used to determine the particle size and particle size distribution of the PMMA particles. The latex was diluted to about 1 wt % with methanol/water mixture (weight ratio = 70/30). 1 drop of the diluted latex was put on a aluminum stub and dried in a hood at room temperature. The accelerating voltage applied was 1 kV, and no coating procedure was applied. For the film-forming poly(*n*-butyl acrylate) particles, dynamic light scattering (Nicomp 370) was applied to determine the particle size.

Molecular Weight Analysis. The molecular weight distributions of the PMMA and PBA were measured by gel permeation chromatography (GPC, Waters 2487 dual absorbance detector and/or Waters 410 differential refractometer detector). THF was used as the mobile phase. When using the UV detector, polymer samples were measured at a wavelength of 235 nm. The THF flow rate was 1.0 mL/min. Waters HR3, HR4, and HR6 Styragel columns were used. Samples were filtered through a 0.45 μm filter before injection. Polystyrene molecular weight standards with narrow distribution were used for calibration. The following Mark−Howink constants were used to obtain the molecular weights: $K = 14.1$, $\alpha = 0.70$ for PSt, $K = 7.5$, $\alpha = 0.72$ for PMMA,[10] and $K = 11.0$, $\alpha = 0.708$ for PBA,[11] all in THF.

Results and Discussion

Particle Size. Four initiator concentrations (2.5, 5.0, 7.5, and 10.0 mM AIBN) were used in dispersion homopolymerizations of MMA and *n*-BuA. For MMA, narrow particle size distributions were achieved at the two lower initiator concentrations (2.5 and 5.0 mM). For *n*-BuA, relatively narrow particle size distributions were achieved at all initiator concentrations. The results are reported in Table 2 and in Figure 1 as a log−log plot of particle size vs initiator concentration. Note first that under similar reaction conditions (same solvent, stabilizer, initiator, and reaction temperature) the resulting PMMA particles are much larger than the corresponding PBA particles. Second, the dependency of the particle size on initiator concentration is also greater for MMA (0.61) than *n*-BuA (0.25), and both are positive. Prior work gave a similar dependence for MMA;[5] however, a negative dependence was reported for *n*-BuA in contrast to these findings.[9] This difference is likely caused by differing reaction conditions, particularly the composition of the medium, which was 90/10 methanol/water in the prior case compared to 70/30 in this case.

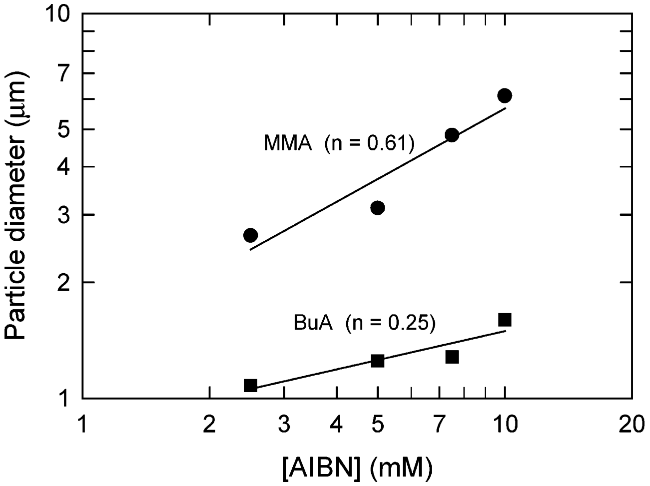

Figure 1. Effect of initiator concentration on particle size in MMA and *n*-BuA dispersion polymerizations.

Kinetics of Dispersion Polymerization. The kinetics of dispersion polymerization of MMA at the four concentrations of AIBN are shown in Figure 2a as the reaction rate and fractional conversion as a function of time and Figure 2b as the reaction rate vs fractional conversion. Figure 3 shows the corresponding results for *n*-BuA dispersion polymerizations. Interesting similarities and differences can be seen in these results.

In general, as might be expected, increasing the initiator concentration increased the reaction rate as seen in both the R_p−time and R_p−conversion profiles. Higher initiator concentrations generate greater radical concentrations in the system. Although it is not clear how the distribution of initiator (or radicals) in the different phases (partitioning of initiator between the continuous and particle phases) affects the kinetics, a higher reaction rate is normally expected with higher initiator concentration. The reaction rate profiles can roughly be divided into three stages either by time or by fractional conversion. First, there is a rapid increase to $R_{p,ini}$; second, a gradual increase to $R_{p,max}$; and third, a gradual decrease to the end of the reaction. The greatest difference between these two systems appears to lie in the second stage rise to a rate maximum, where this occurs more uniformly in the *n*-BuA system. The mechanisms involved in the three stages are briefly discussed as follows.

a. $R_{p,ini}$. Increasing initiator concentration increases the initial reaction rate ($R_{p,ini}$). Since dispersion polymerization indeed starts from a homogeneous solution, theoretically the kinetics of solution polymerization should hold at the beginning of a dispersion polymerization. Lu[12] compared the conversion−time profile of a St dispersion polymerization in ethanol to a solution polymerization in cyclohexane using the same amount of AIBN initiator. The early conversion−time profiles appeared to overlap each other. The conclusion was drawn that dispersion polymerization initially follows the kinetics of solution polymerization and can be described by

$$R_p = k_p[M]\left[\frac{2fk_d[I]}{k_t}\right]^{1/2} \tag{2}$$

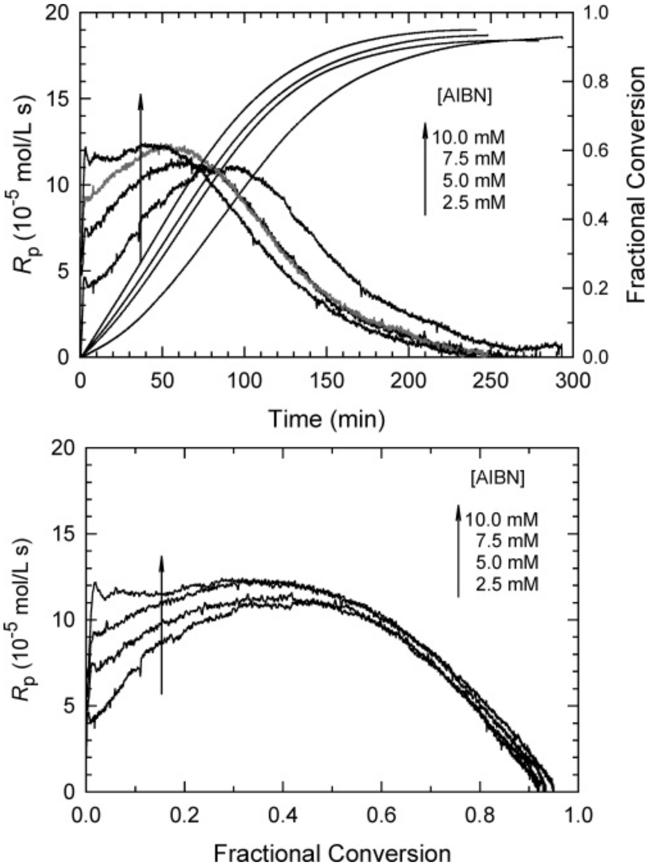

Figure 2. Kinetics of MMA dispersion polymerizations with different AIBN concentrations: (top) reaction rate and fractional conversion vs time and (bottom) reaction rate vs fractional conversion. T_r = 70 °C, methanol/water = 70/30, [PVP K-30] = 20.0 wt % based on monomer, 400 rpm in the RC1 reactor.

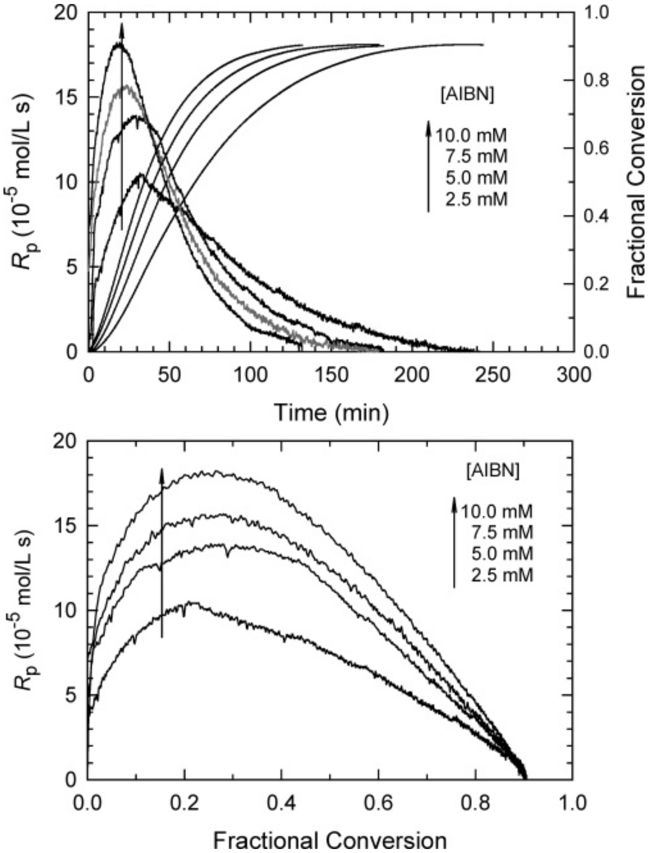

Figure 3. Kinetics of *n*-BuA dispersion polymerizations with different AIBN concentrations: (top) reaction rate and fractional conversion vs time and (bottom) reaction rate vs fractional conversion. T_r = 70 °C, methanol/water = 70/30, [PVP K-30] = 20.0 wt % based on monomer, 400 rpm in the RC1 reactor.

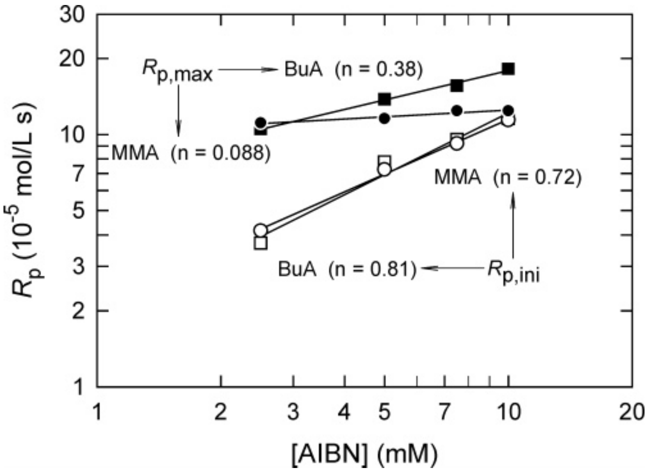

Figure 4. Power dependencies of initial and maximum reaction rate on initiator concentration in MMA and *n*-BuA dispersion polymerizations.

where k_p is the propagation rate constant (L/(mol s)), [M] is the monomer concentration (mol/L), f is the initiator efficiency, k_d is the initiator decomposition rate constant (s^{-1}), [I] is the initiator concentration (mol/L), and k_t is the termination rate constant (L/(mol s)). However, on the basis of observed $R_{p,ini}$ taken from Figures 2 and 3, solution polymerization alone (eq 2) does not appear applicable to this stage in dispersion polymerization. The dependencies of $R_{p,ini}$ on initiator concentration are 0.72 for MMA and 0.81 for *n*-BuA (see Figure 4). This divergence from 0.5 likely indicates that the precipitation of polymer chains begins to occur even prior to reaching $R_{p,ini}$, and the homogeneous system has already become heterogeneous. The growth of polymer chains of length less than their critical chain length (j_{cr}) certainly should follow solution polymerization kinetics. However, the aggregation of oligoradicals to form unstable nuclei will create a heterogeneous system, which would lead to the deviation of early stage kinetics from solution polymerization.

b. $R_{p,ini}$ Increases to $R_{p,max}$. After the initial rapid rise, the reaction rate gradually increases to a maximum. The appearance of the maximum reaction rate in dispersion polymerization is a complex function of the heterogeneous nature of this stage. For dispersion polymerizations that produce narrow particle size distributions, the particle number does not change after a low conversion is achieved (typically considered to be less than 1%). Therefore, the increase in reaction rate does not correspond to an increasing N_p (a long nucleation period). The presence of $R_{p,max}$ has been reported in dispersion copolymerizations of styrene and *n*-butyl acrylate[13] and dispersion polymerizations of styrene in methanol and ethanol.[14] The authors suspected that this was owing to the growth of polymer particles (increased amount of polymer phase and growth therein) or simply the gel effect. In a dispersion polymerization, there are at least two significant polymerization loci: the continuous phase and the polymer particle phase. The reaction rate monitored by calorimetry is the sum of rates from polymerizations in all loci. The polymerization rate in each locus depends on local monomer, initiator, and radical concentrations, the volume of each phase, and propagation and termination rate constants. It has been proposed that there is a third significant polymerization locus, namely the primary particles formed in the continuous phase.[15,16] Radicals that grow to a critical chain length in the continuous phase precipitate to form these unstable nuclei and continue to grow until captured by existing particles.

The dependencies of $R_{p,max}$ on the initiator concentration were evaluated and found to differ significantly, as would be expected by noting the differences in the second stage rate increases for these two systems: for MMA the dependence was 0.09 while for *n*-BuA it was 0.39 (see Figure 4). For *n*-BuA the dependence differs little from that for $R_{p,ini}$, while for MMA the difference is great. Why this is the case is not obvious, but some speculation will be offered in the following. In addition, it should also be noted that the conversions where $R_{p,max}$ occurred for the MMA dispersion polymerizations were all about 40% conversion, while for *n*-BuA, a range from 20% to 30% was found.

The small, nearly negligible $R_{p,max}$ dependence on the initiator concentration found here in MMA dispersion polymerizations is similar to that reported by Lu[17] for dispersion polymerizations of styrene in ethanol. He examined different radical entry mechanisms (collisional,[18,19] diffusive,[1,20] and colloidal[21] entry) adopted from emulsion polymerization by carrying out seeded polymerizations. It was concluded that both diffusive and colloidal entry agree with the observed R_p dependence on the particle size of the seed. In addition, the assumption that the total radical concentration in the continuous phase is proportional to the initiator concentration to the first power might not be applicable for high initiator concentrations owing to increased termination. For MMA seeded dispersion polymerizations, it was shown that colloidal entry is more dominant, which can even cause a reduced reaction rate with increasing initiator concentration.[22] The radical concentration in the polymer phase is a complex function of initiator partitioning, aggregation of polymer chains in the continuous phase, and the rate of radical entry into the particles.

A similar scenario can be applied to the *n*-BuA system. In the systems studied, the critical chain length for *n*-BuA is much shorter than in the MMA system (as reflected in the particle size results; Table 2), which indicates that the aggregation of oligradicals in the *n*-BuA system is not as severe as in the MMA system. Therefore, diffusive radical entry might be the dominant radical entry mechanism in this *n*-BuA dispersion polymerization.

c. Decreasing R_p after $R_{p,max}$. In the third stage, after the maximum, the reaction rate decreases. The decreasing monomer concentration now dominates the reaction kinetics reducing the total reaction rate.

Characterization of Molecular Weights. The evolution of the weight-average molecular weight of the polymers produced in the dispersion polymerizations of MMA and *n*-BuA are shown in Figure 5. It can be seen that increasing the initiator concentration results in a decrease in the molecular weight, and the molecular weight increases with conversion for the MMA polymerizations while a maximum is reached in the *n*-BuA polymerizations at about 40% conversion. With higher initiator concentration, the increase in the molecular weight with conversion becomes less pronounced. These results indicate that in MMA polymerizations higher molecular weight polymer is produced with increasing conversion, while in *n*-BuA polymerizations, higher molecular weight polymer is formed at medium conversions and the molecular weight decreases at high conversions, lowering the average molecular weight of the PBA.

The evolutions of the molecular weight distributions with conversion are shown in Figures 6 and 7. The data have been normalized and scaled with conversion. From Figure 6, it can be observed that for the MMA system the formation of lower molecular weight polymer generally dominates the early stages of the reaction with a shift to higher molecular weight polymers with increasing conversion, as evidenced by the MWD peak shifting to higher molecular weights and/or formation of a shoulder at high molecular weights. Higher initiator concentration results in lower molecular weight and a less pronounced shift toward higher molecular weights. It was also reported that molecular weight increases with conversion for styrene dispersion polymerization in ethanol[12] and MMA dispersion polymerization in supercritical carbon dioxide[23] where the gel effect was considered to be responsible.

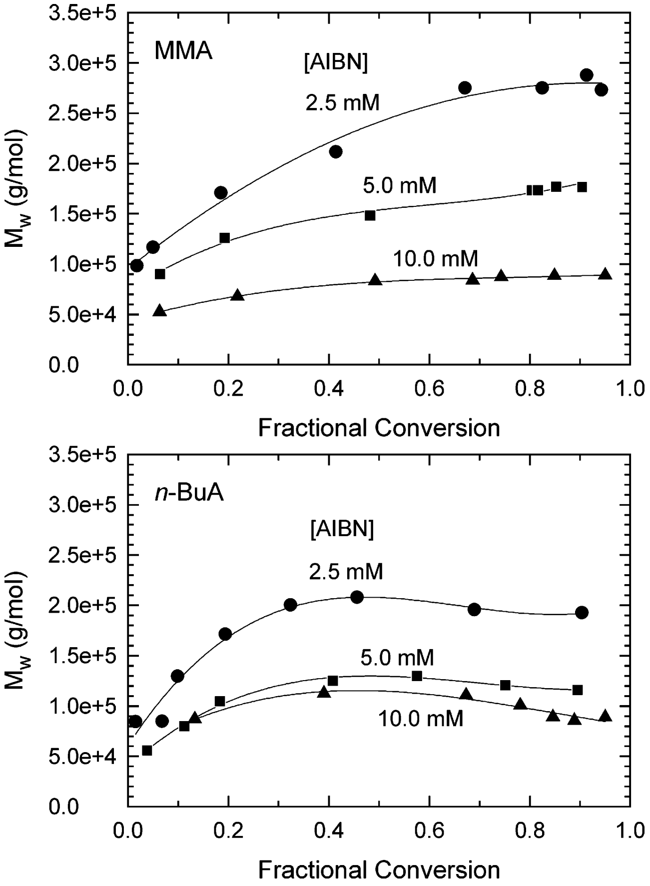

Figure 5. Weight-average molecular weight as a function of conversion obtained in dispersion polymerizations of (top) MMA and (bottom) *n*-BuA with varying initiator concentration; [PVP K-30] = 20 wt % based on monomer, T_r = 70 °C, 400 rpm.

Figure 7 shows the evolution of the MWDs in the *n*-BuA dispersion polymerizations. These differ from those observed in the MMA system. First, low molecular weight polymer was formed in the early stages of the polymerizations, followed by the formation of high molecular weight polymer as evidenced by the appearance of high molecular weight shoulders. This is similar to that observed in the MMA system. However, as the conversion increases, the MWD peak shifts to lower molecular weights, indicating the formation of shorter polymer chains. This is consistent with what is observed in Figure 5 where a maximum weight-average molecular weight appears at ~40% conversion in the *n*-BuA dispersion polymerizations.

Comparing Figures 6 and 7, both similarities and differences in the MWDs between the two polymerization systems can be noted. These features may help in understanding the differences exhibited in the polymerization kinetics. The most obvious difference in the kinetics between these systems is how the rate changes from its initial rise ($R_{p,ini}$) to its maximum ($R_{p,max}$) where

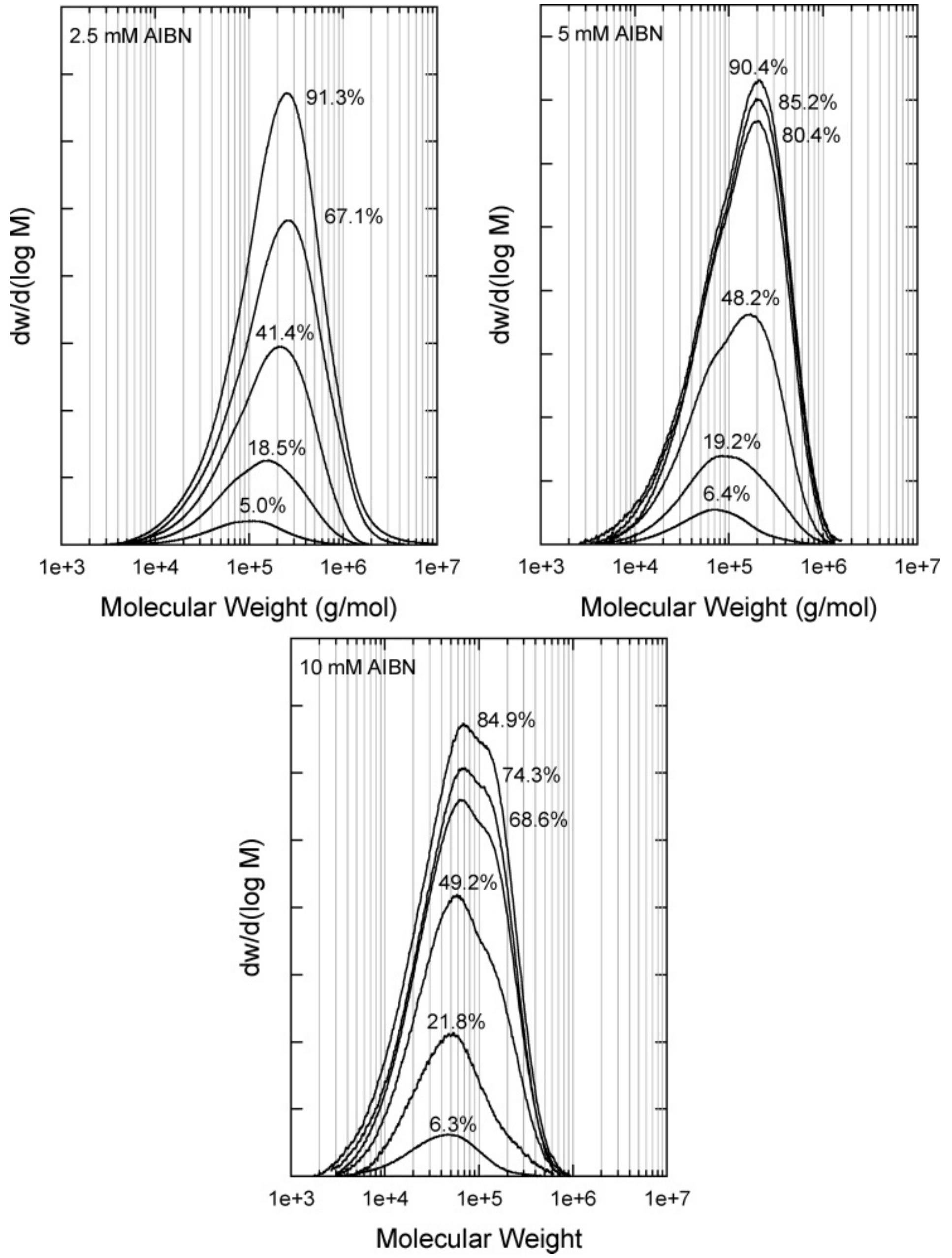

Figure 6. Evolution of molecular weight distributions of PMMA in dispersion polymerizations with AIBN concentrations of 2.5, 5.0, and 10.0 mM.

for all the *n*-BuA dispersion polymerizations the latter was significantly greater than the former and both increased with the initial initiator concentration (Figure 3). However, for MMA, this increase with the initiator level was only true for $R_{p,ini}$, while $R_{p,max}$ only increased slightly if at all (Figure 2). The increase in the rate to a maximum is attributed to a shift in the polymerization locus from the continuous phase (oligomers and unstable nuclei) to the polymer phase (mature particles), which increases in volume as the polymerization proceeds. This shift is believed to be one reason for the increasing molecular weight and increasing reaction rate with conversion seen in both MMA and *n*-BuA dispersion polymerizations. As more polymerization occurs in the polymer phase, the increasing viscosity inside the particles with increasing conversion can cause a decrease in the termination rate constant (gel effect), thus increasing the instantaneous molecular weight. The higher the initiator concentration, the more the polymerization occurs in the continuous phase, resulting in less of a shift in the polymerization locus. As a result, neither the increase in molecular weight or reaction rate is as significant as when the initiator concentration is low (Figures 3 and 5). The large differences between $R_{p,max}$ and $R_{p,ini}$ observed in the *n*-BuA dispersion polymerizations compared to MMA are likely to be caused by a more significant shift in the polymerization locus in the *n*-BuA system, which can be explained by its greater hydrophobicity than MMA. This is also consistent with the shorter critical chain length in *n*-BuA dispersion polymerizations compared to MMA, as implied by the smaller particle size produced under similar conditions.

One might argue that the low molecular weight part of the distributions observed in Figures 6 and 7 results from the short chain polymers produced in the continuous phase. However, as shown in Figures 8 and 9, the molecular weights of the soluble polymers are small compared to the polymer in the particles. These short chain polymers do not contribute much to particle growth. During the particle growth period, unstable nuclei are continuously formed in the continuous phase, and it is believed that these are largely responsible for the lower molecular weight polymer at low conversions. Polymerization

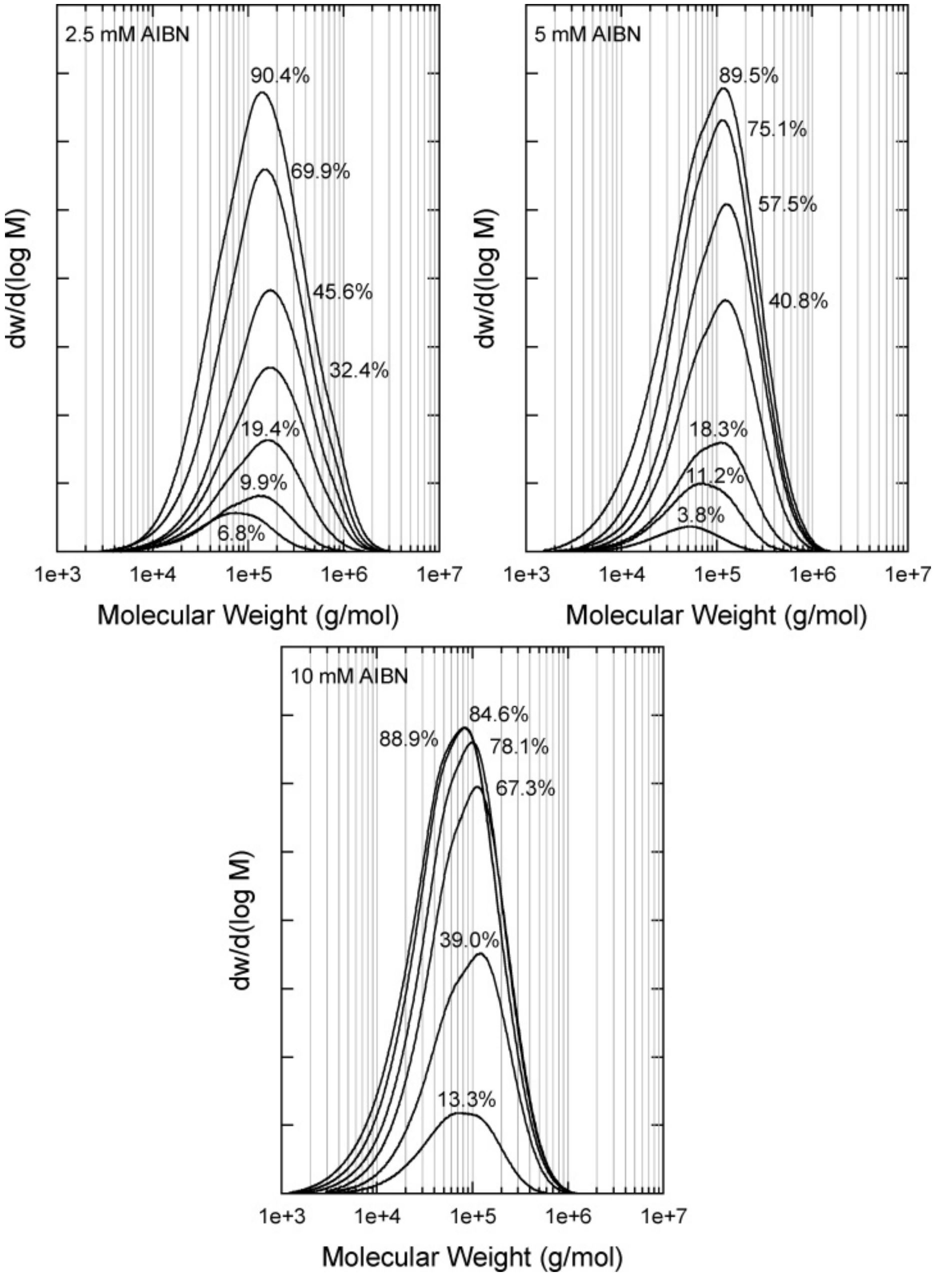

Figure 7. Evolution of molecular weight distributions of PBA in dispersion polymerizations with AIBN concentrations of 2.5, 5.0, and 10.0 mM.

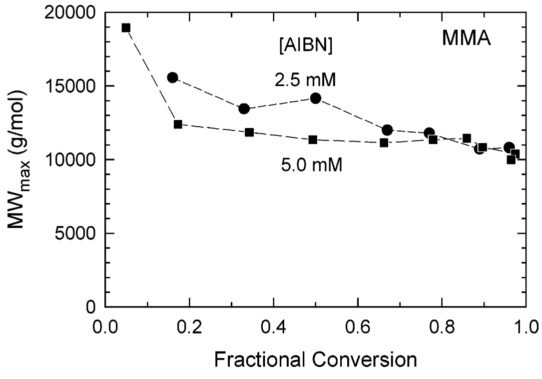

Figure 8. Maximum molecular weights of medium-soluble PMMA in dispersion polymerizations; [I] = 2.5 and 5.0 mM, [PVP K30] = 20 wt % based on monomer, T_r = 70 °C, 400 rpm in the RC1 reactor.

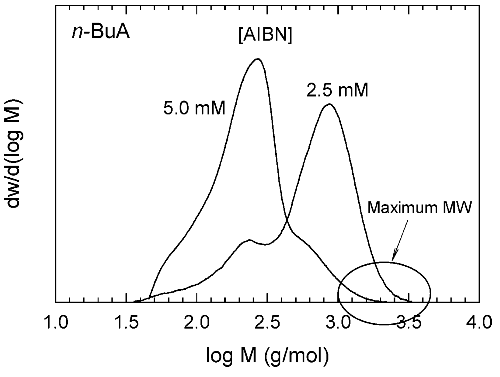

Figure 9. Molecular weight distribution of medium-soluble PBA in dispersion polymerizations; [I] = 2.5 and 5.0 mM, [PVP K30] = 20 wt % based on monomer, T_r = 70 °C, 400 rpm in the RC1 reactor.

inside the polymer particles produces the higher molecular weight polymers.

In dispersion polymerization, particle growth is by polymerization inside the particles and capture of polymer chains as well as unstable nuclei formed in the continuous phase. For PMMA, which is a high-T_g polymer, radical termination in the polymer particles is significantly reduced, owing to the high viscosity inside the polymer particles (gel effect), while much termination occurs in the continuous phase in the aggregation process by which unstable nuclei are produced. However, in PBA particles, the entering oligoradicals are relatively short in length (see Figure 9) and can move more freely in the particles owing to the low T_g of PBA. When the monomer concentration in the particles is relatively high (low conversion), the radicals will react with monomer and grow in molecular weight, which leads to formation of a high molecular weight polymer. However, at high conversion, the monomer concentration in the particles is low, and thus the chains grow more slowly, allowing termination to reduce the molecular weight of the polymer formed.

Critical Chain Length. Figure 8 also indicates the critical chain length in these MMA dispersion polymerizations. It can be seen that the longest medium-soluble PMMA chain is about 100−200 monomer units, which varies with conversion. With increasing conversion, the molecular weight of the PMMA in the continuous phase shows a slight continuous decrease after an initial strong decrease at low conversion. As the polymerization proceeds, the monomer is consumed, and the polymer solubility in the continuous phase should decrease (MMA is a good solvent for its polymer), which would reduce the molecular weight of the polymer that is soluble in the medium. In the *n*-BuA case, the amount of PBA in the continuous phase is very small, and only samples at high conversions (∼90%) were measured. It can be seen from Figure 9 that the soluble PBA chains are short (20−30 monomer units). Recall that smaller particle sizes were produced in the *n*-BuA system compared to MMA (Table 2). It is believed that the size of the medium-soluble chains, which are just one unit less (j_{cr-1}) than that required to form the first crop of nuclei in the nucleation stage of dispersion polymerization, determines the size of nuclei formed in the nucleation stage and thus determines the final particle size.

It should also be pointed out that it is generally believed that the formation of nuclei in the nucleation stage of dispersion polymerization occurs when the polymer chains grow long enough to be insoluble in the medium, and thus the precipitation of these polymers produces the first crop of unstable nuclei. However, the formation of unstable nuclei could also occur by the aggregation of polymer chains that are still soluble in the medium, provided a relatively high concentration is achieved.

Summary

Kinetics studies of methyl methacrylate (MMA) and *n*-butyl acrylate (*n*-BuA) dispersion polymerizations were carried out in a calorimetric reactor. It was found that an increasing initiator concentration increased the reaction rate and decreased the average molecular weight. Three stages were found in the reaction rate profiles of both MMA and *n*-BuA dispersion polymerizations. The reaction rate (initial and maximum R_p) dependencies on initiator concentration differ for the two systems, as well as the evolution of molecular weight with conversion. The molecular weight distributions indicated shifts in the molecular weight populations. The differences were interpreted on the basis of different critical chain lengths, polymer T_g's, radical entry mechanisms, and shifts in the locus of polymerization.

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