Macromolecules **1996,** *29,* 835−841

Kinetics of High-Conversion Free-Radical Polymerization. 1. Understanding Kinetics through Study of Pseudoinstantaneous Molecular Weight Distributions

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Received March 31, 1995; Revised Manuscript Received October 19, 1995[⊗]

ABSTRACT: Study of molecular weight distributions provides a more informative and discriminating approach to uncovering the nature of the gel effect than analysis of rate or molecular weight average data. Analysis of pseudoinstantaneous molecular weight distributions, calculated from cumulative molecular weight distributions, is used in this work to provide new insights into the nature of the gel effect in free-radical polymerization. Pseudoinstantaneous molecular weight distributions from several methyl methacrylate polymerizations have been studied, revealing three distinct instantaneous molecular weight distributions are produced at different times during the polymerization; a single distribution characterizes the low-conversion regime, while two distributions are shown to exist during the high-conversion regime. The evolution of these constituent distributions over the course of the polymerization is described, and the implications of this behavior as it pertains to the gel effect are discussed.

Introduction

Historically, study of the gel effect has concentrated on the increase in the rate of polymerization.[1−11] Indeed it was the increase in rate that was initially detected. Even the term "autoacceleration" refers to a rate phenomenon. Yet the underlying causes result in simulataneous changes to both the instantaneous molecular weight distribution and the rate. The focus of early studies on the polymerization rate was in part a reflection of the limited techniques available for studying polymerization reactions. As methods of measuring molecular weight improved, increased attention was paid to this aspect of the gel effect. However, ability to obtain the complete molecular weight distribution was not available until the development of gel permeation chromatography, and therefore early molecular weight studies were forced to rely on the use of molecular weight averages. The average molecular weights are calculated as the ratio of two moments of the molecular weight distribution. It is the distribution that acts as the source of all the information needed to calculate all the molecular weight averages and the polymerization rate. It is apparent that while the entire quantity of information available can be found in the molecular weight distribution, rates and molecular weight averages represent only a fraction of the overall information.

Relatively few studies reported in the literature have attempted to use molecular weight distributions for kinetic analysis.[12−27] Molecular weight averages along with rate data are commonly reported. Smith et al.[12] and Smith and May[13,14] first appreciated the potential value of molecular weight distribution analysis for kinetic studies. They polymerized styrene and methyl methacrylate to *low conversions* and then compared experimental distributions with theoretically calculated distributions derived from a kinetic model. Analysis was conducted to determine chain transfer constants to initiator and monomer as well as k_p/k_t^2. Westlake and Huang[15,16] analyzed molecular weight distributions to elucidate the relative importance of cationic versus free-radical polymerization in the γ-ray-initiated polymerization of styrene. Braks and Huang[17−19] proposed a method utilizing least squares comparison of experimental and theoretical molecular weight distributions to distinguish an optimal kinetic model in the *low-conversion polymerization* of styrene and methyl methacrylate. Balke[20] and Balke and Hamielec[21] compared experimental and theoretical distributions in the bulk polymerization of methyl methacrylate. This work is notable in that they were the first of the studies described above to focus on the entire conversion regime, and because they recognized the importance of reporting the cumulative molecular weight distributions at various conversions. The potential importance of molecular weight distribution analysis to furthering practical understanding in other areas of polymerization research is illustrated by studies on the use of tubular reactors for the bulk polymerization of methyl methacrylate.[28] Relevant mechanistic and fluid dynamical aspects of the reaction operation would have gone unnoticed without examination of the molecular weight distribution. In extracting information from MWDs, either the number or weight distributions can be examined. Although weight distributions are more commonly used, number distributions are also an important source of information.[29] Gilbert and his colleagues deconvoluted GPC traces of emulsion polymer samples to provide new evidence for the role of coagulative nucleation in systems above the critical micelle concentration. A maximum in the number distribution at low molecular weight in a styrene emulsion polymerization (for a sample taken at the end of the nucleation stage) was interpreted as evidence of coagulative nucleation. It was also demonstrated that the slope of the number distribution can be used to determine the value of the rate constant for chain transfer to monomer in both methyl methacrylate and styrene emulsion polymerizations.

Although the instantaneous and cumulative molecular weight distributions are both a potentially rich data source because they contain information about the polymerization conditions during the evolution of the entire reaction, instantaneous molecular weight distributions provide a complete "snapshot" of what is occurring at any time. This suggests that the instantaneous

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

0024-9297/96/2229-0835$12.00/0

Table 1. Peak Molecular Weights for the Constituent Distributions (Based on $w(M)$ in Ref 34[a]

exptl conditions	low-conv MWD peak MW ($M_{P,L}$)	int-conv MWD peak MW ($M_{P,I}$)	high-conv MWD peak MW ($M_{P,H}$)	$(M_{P,L}M_{P,H})^{0.5}$
0.01 M AIBME, 60 °C	362 000	1 080 000	3 240 000	1 083 000
0.3% AIBN, 70 °C	143 000	568 000	1 700 000	493 000
0.3% AIBN, 90 °C	46 000	186 000	490 000	150 000
0.5% AIBN, 90 °C	43 000	153 000	431 000	136 000

[a] AIBN = azobis(isobutyronitrile); AIBME = dimethyl 2,2-azoisobutyrate.

molecular weight distribution should be a useful tool to gather information about the kinetics of the polymerization as well as to test the validity of any model. Ideally, instantaneous MWDs could be calculated by subtracting the cumulative distribution from a sample taken at the time t from that of the succeeding sample taken at time $t + dt$ where dt is a very small time interval. However, practical considerations dictate the use of “pseudoinstantaneous” MWDs, that is distributions representing a small but finite conversion interval Δx, where Δt may not be small, depending on the availability of data and the ease of collecting sequential samples when the polymerization rate is very high. As the rate of change of the instantaneous conversion becomes greater, more frequent sampling is essential.

In this paper, we describe initial efforts to employ the pseudoinstantaneous molecular weight distributions from methyl methacrylate polymerizations in furthering our understanding of the gel effect. The information obtained in this work will be used in future efforts to develop a kinetic model.

Experimental Data

Cumulative molecular weight distributions spanning a wide range of conversion were obtained from the studies of Huang and O’Driscoll[30] and Balke and Hamielec.[21] Because of the strongly exothermic nature of the polymerization reaction and the sensitivity of the polymerization rate and molecular weight to temperature, great care must be exercised in performing experimental studies to ensure conditions as close as possible to isothermal are maintained. In ampule experiments, the surface:volume ratio of the ampule is a critical parameter in determining the extent of the temperature rise during polymerization.[31] The temperature rise will often be minimal prior to the onset of the gel effect but as the rate increases, the temperature can rise dramatically as the heat generation rate in the ampule exceeds the rate at which heat can be removed by the temperature bath.

The data of Huang and O’Driscoll were generated using specially designed annular ampules possessing a high surface to volume ratio of approximately 10 mm^{-1}. It is expected from consideration of Zhu and Hamielec’s results[31] that temperature rises should be minimal in these ampules. However, there has been some controversy over the isothermality of Balke and Hamielec’s data.[31–33] The evidence presented suggests that the conditions were probably close to isothermal although there is some possibility of heating effects during the gel effect. It should be noted that this data has been extensively used in the literature for studying the gel effect. Because inconsistencies were observed in the molecular weight distribution data at 70 °C with 0.5% AIBN, that data was not included in this study.

Calculation of Pseudoinstantaneous MWDs

This section explains how the pseudoinstantaneous molecular weight distributions were calculated. The raw MWD data (weight fraction as a function of retention volume) were used in the calculations. The decision not to use the actual distributions calculated from calibration curves was made to eliminate the errors associated with calibration, especially in the very high molecular weight regions that are present in many of these samples. The areas of all cumulative distributions were normalized to be proportional to conversion (i.e., normalized to an area of unity, $F(v)$, and then multiplied by conversion, x, to give $xF(v)$). For all data, the measured response is from a differential refractometer. Obtaining a pseudoinstantaneous distribution for a specified conversion interval Δx, bounded by a lower conversion x_1 and a higher conversion $x_2 = x_1 + \Delta x$, requires subtracting the normalized distribution at x_1 from that at x_2. In this manner, the distribution characteristic of each conversion interval can be readily determined.

The polymerization conditions used in the experiments of Hamielec and O’Driscoll are shown in Table 1. As described in the previous section, the calculations of pseudoinstantaneous MWDs were done by subtraction of sequential cumulative molecular weight distributions. No assumptions were made concerning the nature of the distributions, nor was any type of “curve-fitting” approach used. Figure 1 shows all of the pseudoinstantaneous MWDs for the data of Huang and O’Driscoll.[30]

The evolution of pseudoinstantaneous MWDs for all four data sets displayed a common trend. At low conversions, the pseudoinstantaneous MWD of the polymer remains constant with increasing conversion. In other words, the instantaneous MWD is essentially independent of conversion at low conversion and approximates a most probable distribution with polydispersity not greater than 2. Although some variation from decreasing monomer concentration would be expected, it is apparently too small to be detected in this size of interval or the use of logarithmic scales may reduce sensitivity. However, beyond a critical conversion (approximately 15–30% depending on the reaction conditions), a new regime is entered where the pseudoinstantaneous MWD shifts to a higher molecular weight range, indicating the onset of gel effect. The pseudoinstantaneous distributions observed immediately after the onset of the gel effect (call this the “intermediate-conversion instantaneous MWD”) have a peak molecular weight higher than the low-conversion instantaneous MWD and have a polydispersity of approximately 2. However, subsequent pseudoinstantaneous distributions in the intermediate range of conversion are all very broad. At very high conversion, the pseudoinstantaneous distributions generally become narrower. At any given conversion, the pseudoinstantaneous distribution is believed to be a Flory distribution. Therefore the existence of these broad distributions implies that either (1) the conversion interval over which the pseudoinstantaneous MWD was calculated was too large, and during this interval the MWD shifted significantly, or

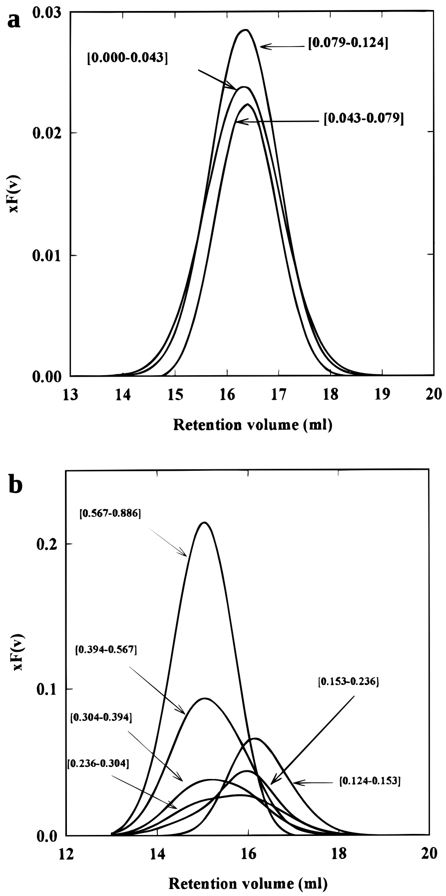

Figure 1. Pseudoinstantaneous MWDs for PMMA data at 60 °C with 0.01 M AIBME (Huang and O'Driscoll) prior to the onset of the gel effect (a) and after the onset of the gel effect (b). The conversion intervals are [a] (1) 0.00−0.043, (2) 0.043−0.079, (3) 0.079−0.124 and [b] (4) 0.124−0.153 (5) 0.153−0.178, (6) 0.178−0.236, (7) 0.236−0.304, (8) 0.304−0.394, (9) 0.394−0.567, (10) 0.567−0.886.

(2) that more than one type of distribution is simultaneously being produced. If the first explanation was valid, the subsequent pseudoinstantaneous MWDs would represent a set of MWDs that were continually shifting to higher molecular weight. However, when the "intermediate-conversion instantaneous MWD" was resolved from all of the subsequent pseudoinstantaneous MWDs, it became apparent that explanation 1 was not consistent with the observations. What was observed was that all subsequent pseudoinstantaneous MWDs were comprised of a *combination* of the intermediate-conversion MWD with another distribution (call this the "high-conversion instantaneous MWD"). Like the intermediate-conversion MWD, the high-conversion MWD also has a polydispersity of approximately 2. Therefore the instantaneous MWD produced after the onset of the gel effect may not consist of a gradually shifting distribution as is generally believed but rather of two characteristic or "constituent distributions" whose relative production rate varies with time. Furthermore, the presence of broad pseudoinstantaneous distributions during the gel effect can be attributed to the combination of these two constituent distributions. The intermediate- and high-conversion MWDs are not adjustable parameters but rather represent a fixed pair of distributions, combinations of which describe all polymer produced after the onset of the gel effect. This observation is not consistent with one type of radical population. Analysis of the subsequent conversion intervals shows that all polymer subsequently produced has a MWD consisting of a combination of these two distinct, constituent molecular weight distributions. Therefore over the entire conversion range from 0 to 100% there are three instantaneous distributions produced: one (low-conversion MWD) produced prior to the onset of the gel effect, and two (intermediate- and high-conversion MWDs) produced after the onset of the gel effect.

For the MMA polymerization data considered in this study, calculation of constituent distribution area versus conversion suggests that polymer produced throughout the entire conversion range consists of three constituent molecular weight distributions. The following procedure can be used to isolate the individual distributions. The low-conversion distribution can be obtained from a low-conversion sample. The intermediate-conversion distribution can be obtained by taking a differential distribution just past the onset of the gel effect (before the high-conversion distribution has appeared). The high-conversion distribution can be obtained by taking a differential distribution at very high conversion, where the growth rate of the intermediate-conversion distribution is at or near zero.

Results

To begin a more detailed examination of the results, consider first the data of Huang and O'Driscoll. These experiments were conducted in specially designed annular ampules to ensure near-isothermal conditions. The calculated pseudoinstantaneous MWDs for the conversion intervals of 0−0.043, 0.043−0.079, and 0.079−0.124 are the same and have a peak molecular weight of 362 000 and polydispersity 1.69. For the interval of 0.124−0.153, however, the pseudoinstantaneous molecular weight distribution differs from that of the three earlier intervals. By taking the difference of the two MWDs at $x = 0.124$ and $x = 0.153$, it was determined that polymer characterized by a distribution with a peak molecular weight of 1 080 000 and polydispersity 1.56 was produced in this interval. This same distribution was also observed in the conversion interval of 0.153−0.178. For the conversion interval of 0.178−0.236, the pseudoinstantaneous MWD again changed. When the intermediate-conversion MWD was subtracted from this distribution, the high-conversion pseudoinstantaneous MWD, centered at 3 240 000 and having a polydispersity of 2.07, was obtained. Analysis of the remaining intervals from 0.236 up to the final conversion of 0.886 revealed that all polymer subsequently produced is characterized by a combination of these two latter pseudoinstantaneous distributions. While the pseudoinstantaneous distribution for the interval 0.567−0.886 does contain polymer from both the intermediate- and high-conversion pseudoinstantaneous distributions, it consists primarily of the high-conversion instantaneous distribution. Figure 1 shows the pseudoinstantaneous MWDs. Figure 2 shows the experimental and calculated overall MWDs obtained by combining the contributions from the three individual pseudoinstantaneous distributions. The MWD data for the other four conversions analyzed (0.236, 0.304, 0.394, 0.567) are equally well described by the same pseudoinstantaneous distributions.

This MWD evolution observed with Huang and O'Driscoll's data (60 °C, 0.01 M AIBME) was also seen with Balke and Hamielec's data (70 °C, 0.3% AIBN; 90 °C, 0.3% AIBN; 90 °C, 0.5% AIBN). Figure 3 shows pseudoinstantaneous MWDs calculated from experimental data (90 °C, 0.3% AIBN) and the overall distri-

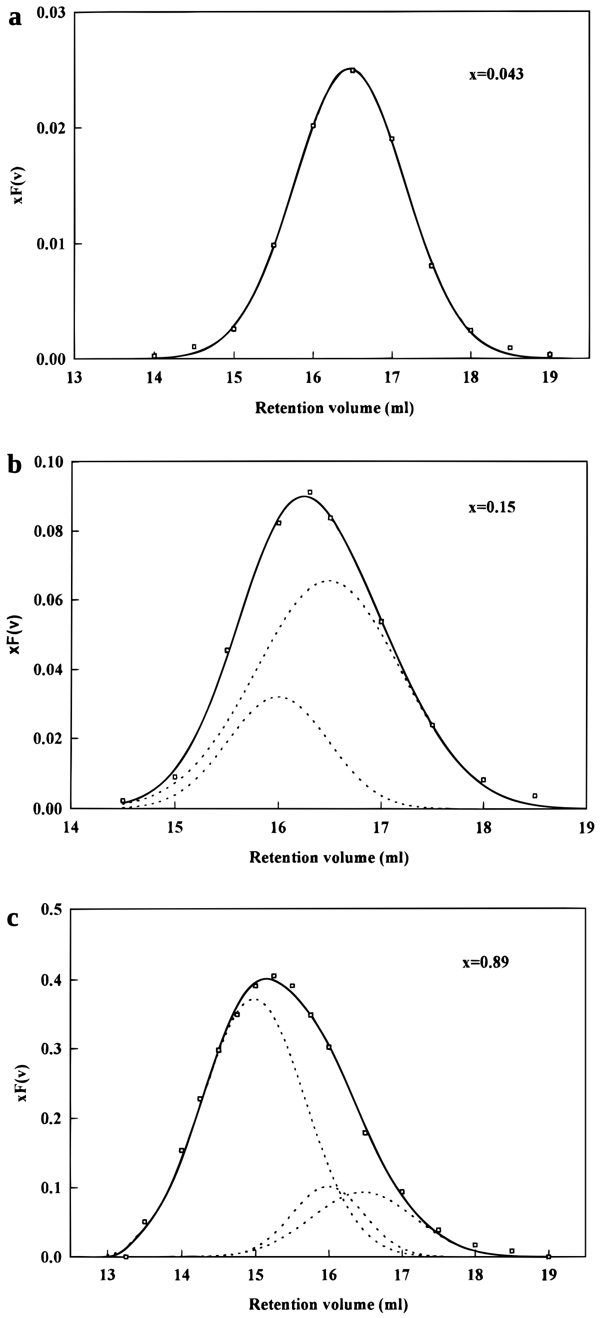

Figure 2. Experimental and calculated MWDs for PMMA data (60 °C, 0.01 M AIBME). Dotted lines represent individual constituent distributions; solid lines represent the sum of constituent distributions. Data points represent the experimental cumulative MWD. (a) Conversion = 0.043. (b) Conversion = 0.153. (c) Conversion = 0.886.

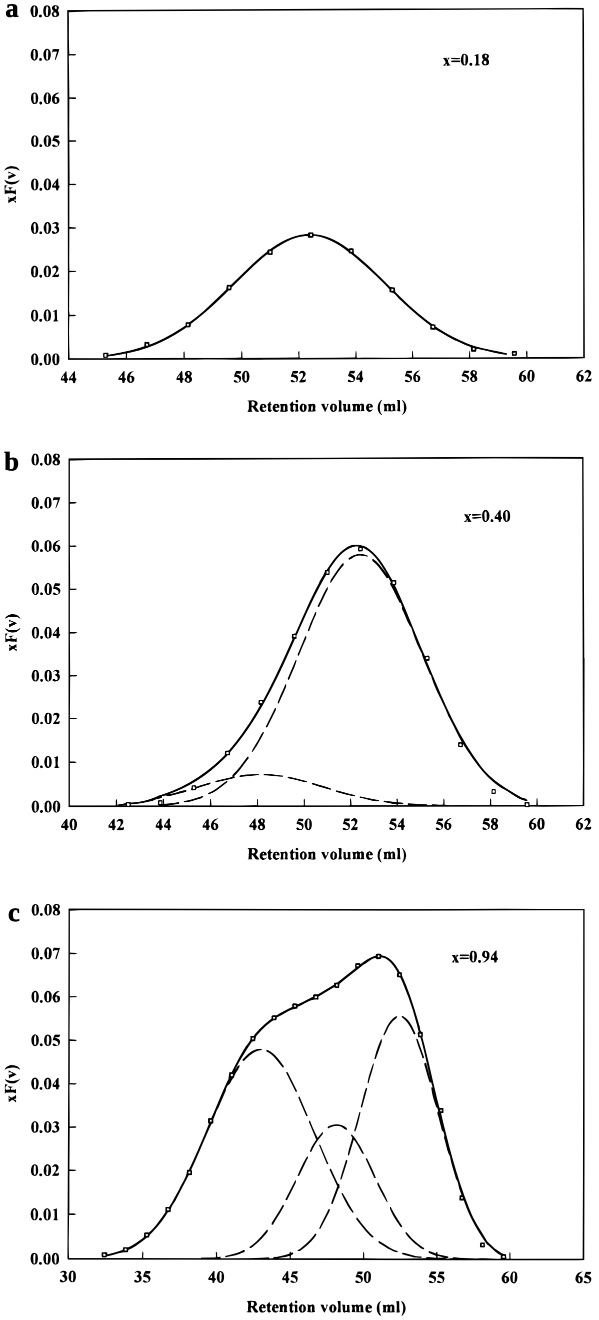

Figure 3. Experimental and calculated MWDs for PMMA data: 90 °C, 0.3% AIBN (Balke and Hamielec). Dashed lines represent individual constituent distributions; solid lines represent sum of constituent distributions. Data points represent the experimental cumulative MWD. (a) Conversion = 0.18. (b) Conversion = 0.40. (c) Conversion = 0.94.

butions obtained by combining the contributions from the three individual distributions, as well as a comparison with the cumulative MWD obtained experimentally. (Again, the MWD data for the other conversions analyzed (0.21, 0.25, 0.65, 0.72) are equally well described by the same pseudoinstantaneous distributions, but have not been shown here because of space limitations). As with Huang and O'Driscoll's data, three fixed, constituent MWDs were produced during the polymerization. The remaining three conditions, not shown here in complete detail for the sake of brevity, follow the same behavior.

Additional information can be obtained by examining the areas and relative growth rates of the three constituent distributions described above. Area represents the total weight of polymer characteristic of a particular constituent MWD. Figures 4 and 5 show plots of areas of each constituent distribution versus conversion for all of the polymerization conditions studied. Comparison of these plots for the various reaction conditions shows how the relative growth rates of the different constituent MWDs vary with the reaction environment. In all cases, the area of the lowest conversion MWD increases linearly to a critical conversion, after which the growth rate declines and eventually ceases. There may be a slight decrease in the area of this low-conversion MWD as conversion continues to increase, perhaps suggesting the occurrence of transfer to polymer. The intermediate- and high-conversion MWDs first appear at about the same critical conversion. The

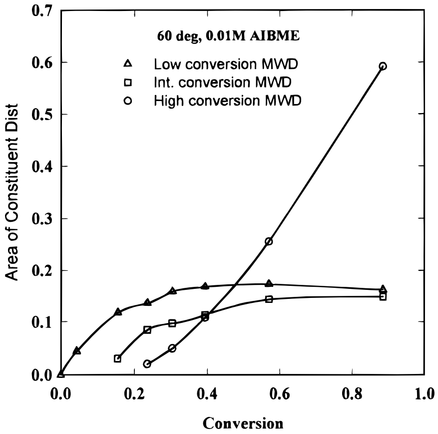

Figure 4. Areas of individual constituent distributions versus conversion for PMMA data: 60 °C, 0.01 M AIBME (Huang and O'Driscoll).

initial appearance of the intermediate- and high-conversion MWDs coincides with the leveling off of the growth rate of the low-conversion MWD. In all cases, the high-conversion instantaneous MWD also increases approximately linearly until the limiting conversion. The data also suggests that the growth rate of the intermediate-conversion instantaneous MWD levels off at high conversions, although more data in the region would be helpful.

The peak molecular weights for each of the three molecular weight distributions for all conditions were calculated and are shown in Table 1. The molecular weights distributions were calculated from the chromatograms using eq 1:[34]

$$w(M) = -[\log_{10} e][dV/d(\log_{10} M)]h(V)/\{M\int h(V)\,dV\} \quad (1)$$

where $w(M)$ is the weight fraction of polymer of molecular weight M, V is the retention volume, and $h(V)$ is the detector response from the chromatogram. In Table 1 the peak molecular weights have been ordered in terms of decreasing peak molecular weight of the low-conversion MWD. The intermediate- and high-conversion peak molecular weights follow the same molecular weight ordering as the low-conversion molecular weight peaks. The high molecular weight distributions lie near or beyond the extremities of the calibration and therefore should be interpreted with caution. The ratio of the high-conversion peak molecular weight to low-conversion peak molecular weight in a given distribution is ~10, the ratio of the intermediate-conversion to low-conversion peak molecular weight is typically ~3, and the ratio of the high-conversion to intermediate-conversion peak molecular weight is also ~3. These values are summarized in Table 2. It can be seen (Table 1) that the peak molecular weights for the low, intermediate, and high conversions ($M_{P,L}$, $Mp_{,I}$, and $Mp_{,H}$ respectively) are approximately related by the expression.

$$M_{P,I} = (M_{P,L}M_{P,H})^{0.5} \quad (2)$$

While we have no explanation for this relationship now, we decided to include it in this paper because it may signify a simple relationship exists to describe the MWD during the gel effect. Our reasoning is as follows. Low-conversion kinetics is described by simple classical kinetics. We have seen evidence that during the gel effect two *invariant* distributions exist, suggesting each

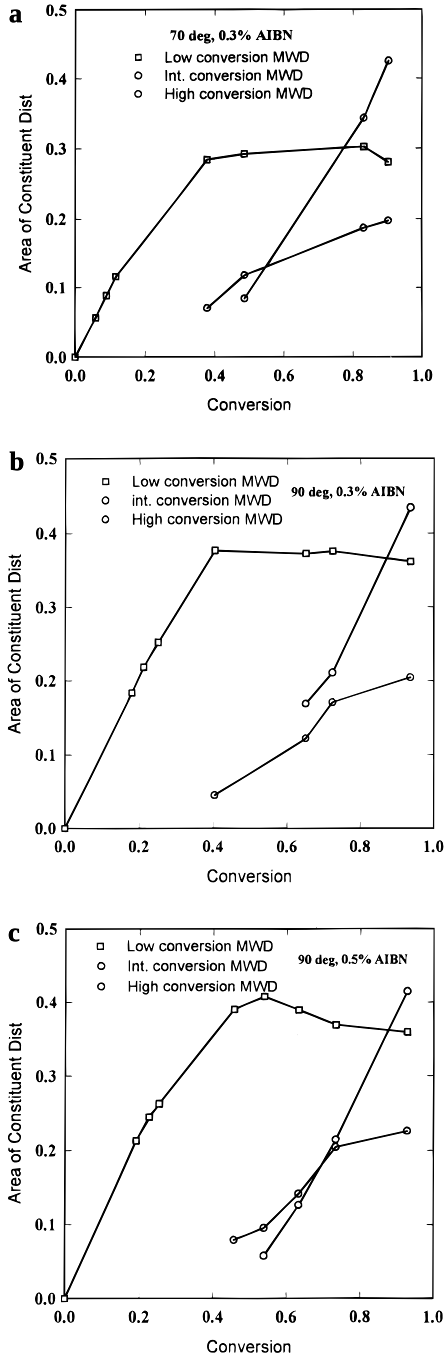

Figure 5. Areas of individual constituent distributions versus conversion for PMMA data (Balke and Hamielec): (a) 70 °C, 0.3% AIBN; (b) 90 °C, 0.3% AIBN; (c) 90 °C, 0.5% AIBN.

Table 2. Ratios of Peak Molecular Weights for the Constituent Distributions

exptl conditions	low:int	low:high	int:high
0.01 M AIBME, 60 °C	1.00:2.98	1.00:8.95	1.00:3.00
0.3% AIBN, 70 °C	1.00:3.97	1.00:11.9	1.00:2.99
0.3% AIBN, 90 °C	1.00:4.04	1.00:10.6	1.00:2.63
0.5% AIBN, 90 °C	1.00:3.55	1.00:10.0	1.00:2.82

of these two distributions could also be described by classical kinetics (with different rate parameters). If a known relationship existed between the various distributions, prediction of molecular weights and rate during the gel effect could be greatly simplified.

Polydispersities of the individual distributions were calculated and are shown in Table 3. These values (1.50−2.54) are all within the range expected for free-radical polymerizations with termination at constant

Table 3. Polydispersities of Each of the Three Constituent Molecular Weight Distributions

exptl conditions	low-conv MWD	int-conv MWD	high-conv MWD
0.01 M AIBME, 60 °C	1.69	1.56	2.07
0.3% AIBN, 70 °C	2.38	1.58	1.62
0.3% AIBN, 90 °C	2.54	1.65	1.99
0.5% AIBN, 90 °C	2.20	1.54	1.82

reaction conditions, allowing for error expected from this type of data analysis procedure, and especially considering the probable error present in calculating very high molecular weights.

Discussion

It has been demonstrated in this work how analysis of instantaneous molecular weight distributions can present a valuable source of information for the study of free-radical high-conversion kinetics. While it has long been recognized that molecular weight increases during the gel effect in MMA polymerizations, it has not been previously realized that the cumulative molecular weight distribution of the polymer is consistent not with a series of gradually increasing instantaneous distributions *but rather with three constituent distributions whose respective molcular weights remain essentially constant for the entire polymerization*. The molecular weight of the individual instantaneous MWDs produced after the onset of the gel effect (the intermediate- and high-conversion instantaneous MWDs) does not vary during polymerization. However, their relative proportion does vary, leading into a continued broadening of the cumulative MWD and increasing number- and weight-average molecular weight as the polymerization progresses. This observation presents an alternative view of the physical and mechanistic nature of autoacceleration as well as providing the basis for a new approach to modeling.

It is worthwhile noting recent developments in the approach to modeling the gel effect. Elaborating upon the concept of short- and long-chain populations first introduced by Cardenas and O'Driscoll,[4] Adams et al.[11] and Russell et al.[35] have proposed that termination events are dominated by short chain−long chain interactions. O'Shaugnessy and Yu[36,37] have theoretically demonstrated that during autoacceleration, most of the polymer produced (that resulting from short−long termination) should have a Flory distribution and that the effective value of k_t is almost independent of chain length for "long" chains. In addition, they conclude the existence of a second distribution of polymer resulting from short−short termination events.

The deduced presence of three distinct molecular weight distributions in MMA polymerizations suggests that three different sets of "kinetic environments" exist. By kinetic environment we mean the complete set of reactant concentrations and rate parameters that determine the MWD of polymer produced at any instant. A continually changing set of reaction parameters would give an infinite set of closely spaced kinetic environments. The types of physical situations which could give rise to three distinct MWDs are now under investigation, including the possibility that the observed behavior could be explained by the presence of two distinct types of polymerization loci, one type present from the onset of the polymerization and a second type arising at or near the onset of the gel effect. At low conversions prior to the onset of the gel effect, classical kinetics can be used to mathematically relate mean chain length, chain length distribution, and rate to the polymerization conditions (e.g., temperature, [I], and [M]). The approximate constancy of the peak molecular weight ratios shown in Table 2 suggests analogous relationships might apply to the intermediate- and high-conversion instantaneous distributions also. If this was the case, analysis of the gel effect and predictive modeling would be greatly simplified. Work on defining the kinetics is ongoing and will be presented in a forthcoming paper.

The existence of a critical conversion which signals a change in the instantaneous molecular weight distribution warrants consideration of a new definition for the onset of the gel effect. O'Driscoll[38] has noted that a complete model of the gel effect must not only describe the increased rate and molecular weight but should also allow for a smooth transition between the low conversion and gel effect regimes. Most current models employ a switch or critical conversion to signify the onset of the gel effect, based on either empirical and/or theoretical considerations. O'Driscoll et al.[39] suggested that the onset of the gel effect be defined as that conversion at which the termination rate parameter k_t has a maximum value, arising from the combination of an increasing segmental termination rate and a decreasing translational termination rate. *We propose that the onset of the gel effect be considered as that point during the polymerization at which the low-conversion MWD switches to the intermediate-conversion MWD.* By taking samples with increased frequency near the onset point, the location of the onset conversion could be determined with any desired level of accuracy. This approach would also be useful in clarifying when the intermediate-conversion MWD first appears relative to the first appearance of the high-conversion MWD and relative to the cessation in growth of the low-conversion MWD. The answers to these questions are critical in developing improved kinetic models.

Analysis of molecular weight distributions also presents an opportunity to better quantify kinetic phenomena such as transfer to polymer and branching. Some of the MMA results showed slight decreases in the areas of the low-conversion MWD, signifying the possible presence of transfer to polymer. A broader database could provide additional information on the effects of factors such as temperature, molecular weight, or initiator concentration on the rate of transfer to polymer.

Conclusions

Analysis of "pseudoinstantaneous" molecular weight distributions, obtained from cumulative molecular weight distributions, has been used to provide new insights into the nature of the gel effect. At low conversions, the pseudoinstantaneous MWD is essentially independent of conversion and approximates a most probable distribution. The instantaneous MWD produced after the onset of the gel effect consists of *two* characteristic or "constituent distributions". These two distributions, which we have called the "intermediate-conversion MWD" and "high-conversion MWD", represent a fixed pair of distributions, combinations of which describe all polymer produced after the onset of the gel effect. Like the low-conversion MWD, these two distributions approximate a most probable distribution. This observation presents a new view of the physical and mechanistic aspects of autoacceleration which could be used in development of a kinetic model.

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MA950446D