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A Method for Online Monitoring of Polydispersity during Polymerization Reactions

Wayne F. Reed

Physics Department, Tulane University, New Orleans, Louisiana 70118

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ABSTRACT: Building on a recently introduced technique for continuous online monitoring of absolute weight-average molecular weight M_w of polymers during polymerization reactions, a method is introduced here for finding a useful approximation to the polymer mass distribution and moments at each instant during the reaction. The method is based on finding the instantaneous weight-average mass at each instant, $M_{w,inst}$, from an expression involving the derivative of the cumulative M_w, which is directly monitored online. The method is restricted to chain growth polymerization where individual chains are produced and terminate rapidly compared to the overall time it takes for complete monomer conversion to polymer. Data from two different polymerization experiments that were monitored online were then analyzed. One of these experiments is from a reaction for poly(vinylpyrrolidone), which produced a bimodal population, and the other from a reaction that produced a broad, unimodal distribution. Finally, other possibilities for online polydispersity measurements are briefly discussed.

Introduction

The quest for reliable online methods for measuring the absolute mass of polymers during polymerization reactions is being driven by both fundamental and economic considerations. At the level of bench scale chemistry, online monitors can help guide the synthesis of new materials, optimize the production of traditional ones, and provide direct understanding of kinetics and mechanisms. At the industrial scale, such monitoring is expected to result in considerable savings in cost, energy, and raw materials as well as to ensure higher, more uniform product quality.

A technique for continuous online monitoring of the absolute weight-averaged molecular mass at each instant in time $M_w(t)$ of polymers during polymerization reactions was recently introduced by Florenzano et al.[1] The technique uses continuous, automatic reactant dilution, combined with time-dependent static light scattering (TDSLS), and an appropriate concentration detector(s). Additionally, an online viscometer was used to follow polymer reduced viscosity η_r as the polymerization proceeds. Although the authors mentioned the possibility of estimating a certain ratio of mass distribution moments (M_w and viscosity averaged mass) to obtain an online measure of the polydispersity as polymerization proceeded, the technique was not significantly developed.

Determination of equilibrium polymer molecular mass distributions is generally considered to fall in the province of separation techniques such as size exclusion chromatography.[2,3] Other equilibrium techniques such as dynamic light scattering have been used with some success for equilibrium distribution determinations.

The goal of the current work is to introduce a method that can be used for online estimation of the evolving mass distribution and moments during polymerization reactions from the instantaneous weight-averaged molecular mass, $M_{w,inst}$, which can be computed from the derivative of the directly monitored M_w, which, for chain-growth reactions, represents the cumulative M_w of all chains produced up to a given instant. While the method is too approximate to rival the detailed distributions obtained by equilibrium separation techniques, it should be a useful tool both for modeling polymerization kinetics and for online monitoring of population broadening, production of multimodal populations, etc.

Although the author is unaware of previous online, continuous measurements of polydispersity, the general area of polymerization monitoring has received significant attention and has a fairly long history. One of the first attempts to follow rates and M_w is due to Flory,[4] who manually withdrew aliquots from a glycol/dibasic acid polyesterification reaction every 10 min and performed a KOH titration to estimate molecular weights and rate constants. Bresler et al.[5] were able to make periodic ESR measurements to follow radical concentrations in homogeneous polymerization reactions of methyl methacrylate and vinyl acetate. Shen and Tian subsequently improved on the ESR technique and were able to simultaneously measure radical concentration and monomer conversion in methyl methacrylate polymerization at intervals a few minutes apart.[6] Ballard and van Lienden[7] used literature values of polymer densities to estimate initial polymerization rates of vinyl monomers by metal compounds using a dilatometer. The dilatometer is frequently used as an empirical means of following polymerization reactions.

Real-time monitoring of polymerization is a more recent development. Infrared,[8−13] ultraviolet (UV),[14,15] and fluorescence[16] monitoring are proving particularly useful for measurements of monomer conversion and process completion. Fluorescence techniques are also being used for monitoring curing reactions of epoxies.[17,18] IR studies have been employed to estimate rheological properties,[19] whereas direct rheological techniques are being used to estimate molecular weight online.[20,21] Monitoring post-pulse processes in laser-induced polymerization has also been recently reported.[22] Laser flash photolysis has been used to monitor fast, photoinduced laser polymerization kinetics in surfactant vesicle systems.[23,24]

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Summary of the Online Monitoring Technique

Reference 1 introduced an automatic, continuous method for monitoring polymerization reactions. The authors continuously withdrew about 40 μL/min from a reactor (filled with reacting vinylpyrollidinone in that case) and used a conventional mixing pump to dilute this with about 1 mL/min of pure water. This diluted mixture, typically containing a combined monomer and polymer concentration of 0.005 g/cm^3, flowed through a train of detectors comprising a single angle light scattering flow chamber that the authors developed, a home-built single capillary viscometer, a differential refractometer (for determining the combined monomer and polymer concentration), and an ultraviolet absorption photometer to determine the remaining monomer content and hence also the degree of monomer conversion. The absolute light scattering value at each instant was combined with the polymer concentration to obtain the cumulative weight-average mass $M_w(t)$ at each moment. The concentration and viscosity data were likewise combined to yield the cumulative reduced viscosity at each point.

The method has recently incorporated an improved, home-built multiangle light scattering chamber, and more attention has been given to time response.[25]

Obtaining $M_{w,inst}$ from M_w

In the following a method for obtaining approximate mass distributions is obtained from using the derivative of the cumulative weight-average mass M_w. This involves first finding the *instantaneous* weight-averaged mass $M_{w,inst}$. $M_{w,inst}$ is the weight-average mass of the incremental population of polymer chains produced during a small conversion interval. Finding $M_{w,inst}$ is conceptually equivalent to finding the latest term summed into a running average, given the current and previous values of the running average; e.g., if we know the value of the average test grade for n students and then know the new average after another grade has been averaged in, we can immediately compute this latter grade that changed the average to its new value.

The online monitoring technique of ref 1 provides a continuous record of the absolute value of $M_w(t)$, which can also be expressed in terms of conversion, $M_w(f)$, where $f(t)$ is the fraction of monomer converted to polymer at any instant t

$$f(t) = C(t)/C_{m,0} \tag{1}$$

where $C_{m,0}$ is the initial monomer concentration, and $C(t)$ is the continuously measured polymer concentration. At a given degree of conversion f, there will be a total concentration of polymer given by

$$C(f) = \int_0^\infty c(M,f)\,\mathrm{d}M \tag{2}$$

where $c(M,f)\,\mathrm{d}M$ is the accumulated concentration of polymer in the mass interval M to $M + \mathrm{d}M$ at a degree of conversion f. As polymerization proceeds, $c(M,f)$ changes, the details of which depend on the detailed kinetics and conditions of the reaction. Defining $g(M,f)$ to contain this kinetic information, we have

$$\frac{\mathrm{d}c(M,f)}{\mathrm{d}f} = g(M,f) \tag{3}$$

Useful properties of $g(M,f)$ include

$$C_{m,0} = \int_0^\infty g(M,f)\,\mathrm{d}M \tag{4}$$

which is obtained by changing the order of differentiation and integration, and using eqs 1 and 2, and

$$fC_{m,0} = \int_0^f\int_0^\infty g(f',M)\,\mathrm{d}M\,\mathrm{d}f' \tag{5}$$

which follows from the previous equation.

In chain-type polymerization chains are normally formed quickly and then terminate, so that there is a continuous buildup of “dead chains” that make up the total polymer mass distribution. Hence, for a given degree of conversion f, the $M_w(f)$ measured online is given by

$$M_w(f) = \frac{\int_0^f\int_0^\infty Mg(M,f')\,\mathrm{d}M\,\mathrm{d}f'}{\int_0^f\int_0^\infty g(M,f')\,\mathrm{d}M\,\mathrm{d}f'} \tag{6}$$

$M_{w,inst}(f)$ is the weight-average mass of the polymer produced during the conversion interval f to $f + \mathrm{d}f$. Using the definition of $g(M,f)$,

$$M_{w,inst}(f) = \frac{\int_0^\infty Mg(M,f)\,\mathrm{d}M}{\int_0^\infty g(M,f)\,\mathrm{d}M} \tag{7}$$

Using eqs 4 and 5 allows $M_w(f)$ to be expressed as

$$M_w(f) = \frac{\int_0^f M_{w,inst}(f')\,\mathrm{d}f'}{f} \tag{8}$$

This equation can be cross-multiplied and differentiated immediately to yield

$$M_{w,inst}(f) = f\frac{\mathrm{d}M_w(f)}{\mathrm{d}f} + M_w(f) \tag{9}$$

Obtaining Relative Mass Distributions and Moments from $M_{w,inst}$

Knowledge of $M_{w,inst}(f)$ allows the evolution of the relative polydispersity during a polymer reaction to be monitored, without any model-dependent assumptions. “Relative polydispersity” here means that the polydispersity at each instant is relative to that at the outset of the reaction, and no account is taken of the width of the polymer population produced in each instant. It is hence possible to see how a population broadens, becomes bimodal, etc., with this treatment. The absolute polydispersity and population distribution can only be computed online via a model. This is treated in the next section.

In the relative polydispersity treatment, when $M_{w,inst}(f)$ is a monotonically increasing or decreasing function,

$$c(M_{w,inst},f) = C_{m,0}\left|\frac{\mathrm{d}f}{\mathrm{d}M_{w,inst}}\right| \tag{10}$$

so that

$$c(M_{w,inst},f) = \frac{C_{m,0}}{\left|2\frac{\mathrm{d}M_w}{\mathrm{d}f} + f\frac{\mathrm{d}^2M_w}{\mathrm{d}f^2}\right|} \tag{11}$$

This expression gives the relative polymer mass distribution as it evolves as a function of conversion f (or time). The relative values of all the usual averages, M_n, M_w, and M_z, as well as any others, can be found from this. The notation $c(M_{w,inst},f)$ is used to emphasize that this distribution function exists only over the domain of the values of $M_{w,inst}$ produced up to conversion f.

As will be demonstrated below with real data, finding $M_{w,inst}(f)$ involves taking derivatives of experimental data with noise, and $c(M_{w,inst},f)$ involves both the first and second derivatives of these data. Hence, a more approximate scheme will be used below in which finite data intervals are used to smooth out noise, and a histogram of the distribution in eq 11 is found.

Converting the equation for $M_{w,inst}(f)$ into discrete form gives the representation

$$M_{w,inst}(f_i) = f_{i-1}\left[\frac{M_w(f_i) - M_w(f_{i-1})}{\Delta f_i}\right] + M_w(f_i) \quad (12)$$

where f_i is the conversion at the ith sampled point during online monitoring, and $\Delta f_i = f_i - f_{i-1}$.

The discrete points for $M_{w,inst}(f_i)$ are amenable to a histogram representation, if desired, where the sum of the Δf_i falling within a given range of $M_{w,inst}$ is plotted vs the average value of the range. In this case, the monotonicity of $M_{w,inst}(f)$ is no longer required.

It is useful to express the averages $M_n(f)$ and $M_z(f)$ in terms of their respective instantaneous averages $M_{n,inst}(f)$ and $M_{z,inst}(f)$, as was done for $M_w(f)$ in eq 8. $M_{n,inst}$ is given by

$$M_{n,inst}(f) = \frac{\int_0^\infty g(M,f)\,dM}{\int_0^\infty \frac{g(M,f)}{M}\,dM} = \frac{C_{m,0}}{\int_0^\infty \frac{g(M,f)}{M}\,dM} \quad (13)$$

similarly, $M_{z,inst}(f)$ is given by

$$M_{z,inst}(f) = \frac{\int_0^\infty M^2 g(M,f)\,dM}{\int_0^\infty M g(M,f)\,dM} = \frac{\int_0^\infty M^2 g(M,f)\,dM}{C_{m,0} M_{w,inst}(f)} \quad (14)$$

where eq 7 above has been used to simplify the denominator in the middle term of the above equation.

$M_n(f)$ and $M_z(f)$ can now be expressed in terms of their instantaneous values. By definition,

$$M_n(f) = \frac{\int_0^\infty c(M,f)\,dM}{\int_0^\infty \frac{c(M,f)}{M}\,dM} = \frac{C(f)}{\int_0^f \int_0^\infty \frac{g(M,f')}{M}\,dM\,df'} \quad (15)$$

where eq 2 has been used for the numerator and the order of integration in the demoninator has been interchanged, which is valid, since f and M are independent variables. Using eqs 1 and 13,

$$M_n(f) = \frac{f}{\int_0^f \frac{df'}{M_{n,inst}(f')}} \quad (16)$$

$M_z(f)$ is by definition

$$M_z(f) = \frac{\int_0^\infty M^2 c(M,f)\,dM}{\int_0^\infty M c(M,f)\,dM} = \frac{\int_0^\infty M^2 \int_0^f g(M,f')\,df'\,dM}{C(f)\,M_w(f)} \quad (17)$$

Using eq 14 and interchanging the order of integration in the numerator yields

$$M_z(f) = \frac{\int_0^f M_{z,inst}(f')\,M_{w,inst}(f')\,df'}{f M_w(f)} \quad (18)$$

As it stands, there is no way of directly measuring $M_{n,inst}$ and $M_{z,inst}$. If $M_{w,inst}(f)$ is substituted for these terms in eqs 16 and 18, then the relative evolution of $M_n(f)$ and $M_z(f)$ will be measured, and the relative changes in the traditional polydispersity indices, M_z/M_w and M_w/M_n, can also be followed. To have absolute measures of these quantities requires introduction of a model. This is briefly considered in the next section.

Considerations on the Widths of Instantaneous Distributions

If we know, or have a model for, the polydispersity of the instantaneous population at any instant of conversion f, $p_1(f)$, such that

$$p_1(f) = \frac{M_{w,inst}(f)}{M_{n,inst}(f)} \quad (19)$$

then the experimentally determined values of $M_w(f)$ can be used to determine $M_n(f)$:

$$M_n(f) = \frac{f}{\int_0^f \frac{p_1(f')\,df'}{M_{w,inst}(f')}} \quad (20)$$

Likewise, if we know or have a model for the instantaneous ratio M_z/M_w

$$p_2(f) = \frac{M_{z,inst}(f)}{M_{w,inst}(f)} \quad (21)$$

then

$$M_z(f) = \frac{\int_0^f p_2(f')\,M_{w,inst}(f')^2\,df'}{f M_w(f)} \quad (22)$$

Hence, if we have a model for the instantaneous polydispersity at every point, it is possible to compute all the averages of the population. For many chain growth polymerizations where the dominant termination mechanism is disproportionation, the population of dead chains produced in a short time interval follows the geometric distribution

$$N_i = A(1 - q)q^{i-1} \quad (23)$$

where N_i is the number of chains of length i produced in a given interval, A is a normalization constant, and q is the probability of a chain propagating at every point versus terminating. Knowledge of any moment (higher than the zeroth) yields the complete distribution. $q(f)$, the value of q at conversion f, can be found from $M_{w,inst}(f)$ by

$$M_{\mathrm{w,inst}}(f) = \frac{1 + q(f)}{1 - q(f)}m \qquad (24)$$

where m is the monomer mass. The other common moments of the distribution are related to q by

$$M_{\mathrm{n,inst}}(f) = \frac{1}{1 - q(f)}m \qquad (25)$$

and

$$M_{z,\mathrm{inst}}(f) = \frac{q(f)^2 + 4q(f) + 1}{(1 - q(f)^2)} \qquad (26)$$

For long chains (that is above about 20 units), the well-known averages of this population stand in the ratio M_z:M_w:M_n = 3:2:1, so that for all f

$$p_1(f) = 2 \quad \text{and} \quad p_2(f) = 1.5 \qquad (27)$$

Hence, for chain type polymerizations where relatively long chains are produced—which is a very frequent case—the absolute values of M_z, M_w, and M_n can be computed at every moment from the online values of $M_{\mathrm{w,inst}}(f)$ using eqs 20 and 22. In fact, in the long chain limit, the model-dependent, cumulative values of M_z and M_n are obtained at every point by simply multiplying the values of $M_z(f)$ and $M_n(f)$, from eqs 20 and 22, uncorrected for polydispersity (i.e., $p_1(f) = p_2(f) = 1$) by 1.5 and $M_n(f)$ by 0.5, respectively.

Representation of $M_{\mathrm{w,inst}}$ in the Time Domain

It is stressed that in the online monitoring technique both $M_w(t)$ and conversion are being simultaneously and continuously monitored, so that representations in both time and f can be simultaneously made with no additional information. Since $f(t)$ is known from the online monitoring technique, $M_{\mathrm{w,inst}}(t)$ can be represented at each point in time by

$$M_{\mathrm{w,inst}}(t) = f(t)\frac{\mathrm{d}M_w(t)}{\mathrm{d}t}\frac{\mathrm{d}t}{\mathrm{d}f} + M_w(t) \qquad (28)$$

$M_n(t)$ and $M_z(t)$ in eqs 20 and 22 can be computed by replacing df' by (df'/dt') dt' in the respective integrals.

Application to Two Data Sets for Online Monitoring

1. A Bimodal Distribution. In ref 1, Florenzano et al. found the remarkable result that, using a hydrogen peroxide initiator, M_w remained constant throughout the poly(vinylpyrrolidone) (or PVP) reactions tested. To vary from this, one reaction was tried in which a second round of initiator was injected after the reaction had already run for awhile. Such a second addition of initiator is often referred to as a reaction “booster”. It was expected and verified by size exclusion chromatography (SEC) that this produced a bimodal distribution (Figure 10, ref 1).

Figure 1 shows the M_w data from ref 1 vs conversion. Because the booster added noise to the data in ref 1, the data shown in Figure 1 have been smoothed by rejecting spuriously high light scattering points due to bubbles, contaminants, etc. Even with this smoothing, the point-to-point fluctuations are far too great to permit taking useful first and second derivatives of the function from point-to-point, as specified by eqs 9−11.

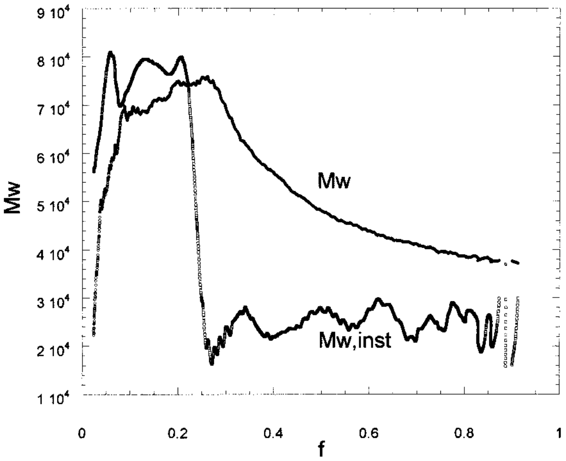

Figure 1. M_w vs f (fractional monomer conversion) for data from reaction 7 in Florenzano et al.[1] Also shown is $M_{\mathrm{w,inst}}$ computed from M_w using the end-point averaging scheme (200 point intervals, 80 points on each end), according to the discrete procedure of eq 12.

In light of this, there are several ways to approach the data analysis. One would be to fit a functional form to the data and then take the exact derivatives indicated in eqs 9−11. Since the functional form is not obvious, and choosing an arbitrary one could introduce considerable artifacts when first and second derivatives are taken, an approximate approach using intervals is taken here. We do not attempt to explore other data analysis schemes at this point, nor enter into error analysis, since the object of this work is to introduce the overall method. Full implementation of the online polydispersity method, however, will require technical study of various possibilities and perhaps will rely on more than one type of averaging and differentiating routine to maintain cross-checks on values and monitor error bars. Current microcomputer computational speeds are such that large numbers of calculations can be made while data acquisition is in progress.

In the analysis here, two techniques were used. Linear fits were made over small conversion intervals in Figure 1, typically around Δf of 0.01−0.05 increments. Different weighting schemes were considered. The second scheme involved defining an interval of points in f, and averaging a subset of these at the beginning and end of the interval, and taking the slope from the resulting interval end points. In this approach both $M_w(f)$ and f itself are averaged, because there is also noise in f, since it depends on the signal from an ultraviolet spectrophotometer in this case.

It is noted that in the experiment, data were collected at equal time intervals. Hence, there is a higher density of data points per conversion interval at the beginning and end of the reaction, when f is changing more slowly in time.

In this instance the second method gave slightly better results, although there was no essential difference. The $M_{\mathrm{w,inst}}(f)$ thus computed is also shown in Figure 1. A total of 200 points were taken per averaging interval. There appears to be a very early generation of short chains, although this might be artifactual, since at early conversion $M_w(t)$ is computed from the ratio of two very small signals (scattering intensity and polymer concentration), each with significant noise. This is followed by a period of production of approximately constant chains of M_w around 70 000−80 000 g/mol, until the initiator boost was made at f =

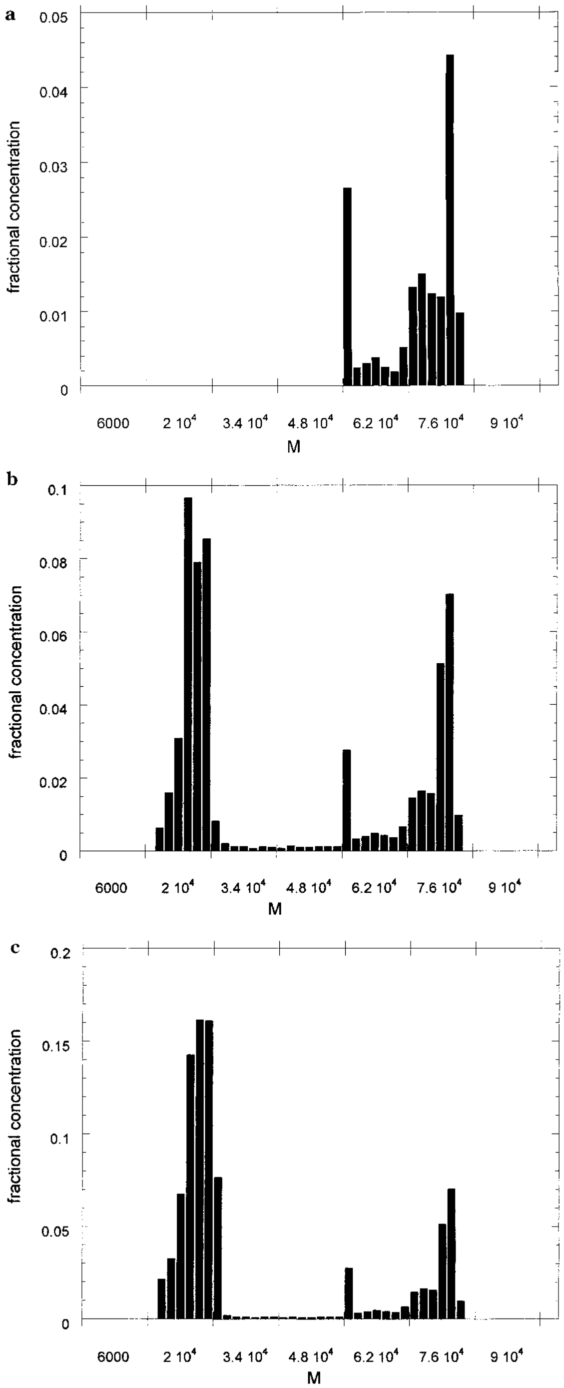

Figure 2. Histograms of mass distribution at different conversion points: (a) $f = 0.2$, (b) $f = 0.6$, and (c) $f = 0.9$.

0.2, after which a fairly constant population of chains between 20 000 and 30 000 g/mol is produced until the end of the reaction. These values correspond well to the values of the bimodal SEC histogram shown in Figure 10, ref 1.

What is remarkable is that it is not obvious from the $M_w(f)$ data of Figure 1 that a well-defined bimodal population is involved. $M_{w,inst}(f)$ in Figure 1, however, makes this immediately clear.

A histogram approach was taken to finding the distribution $c(M_{w,inst},f)$ rather than using the first and second derivatives of eqs 9–11. A set of mass intervals was defined and the $M_{w,inst}(f)$ data sorted into it, weighted by the Δf between sequential points. Figure 2a–c shows the histogram of the evolving polymer population, determined this way, at selected points in the reaction; $f = 0.20$, 0.60, and 0.90. The bimodality is clearly seen, which is consistent with the SEC results in ref 1.

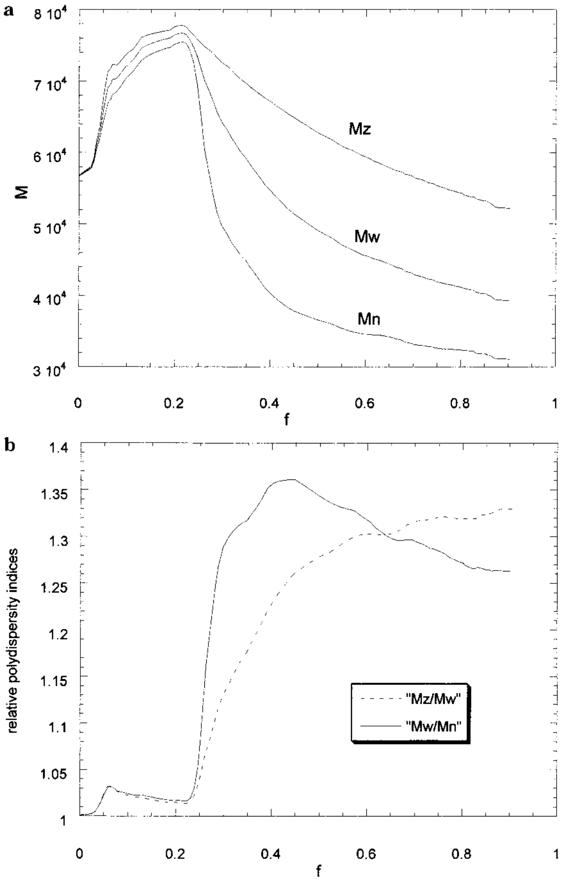

Figure 3. (a) Evolution of M_n, M_w, and M_z using eqs 8, 20, and 22, in conjunction with the $M_{w,inst}(f)$ curve from Figure 1b, and no correction for instantaneous polydispersity (i.e., with $p_1(f) = p_2(f) = 1$). (b) Traditional polydispersity ratios M_z/M_w and M_w/M_n from (a).

Taking the moments of a bimodal distribution is not very meaningful, since the averages produced are merely those between the two populations, and no actual masses in the distribution correspond to them. Nonetheless, Figure 3a shows the evolution of the relative M_n, M_w, and M_z by substituting $M_{w,inst}(f)$ from Figure 1 into the average of eqs 8, 20, and 22, respectively, with $p_1(f) = p_2(f) = 1$. The behavior of M_w in Figure 3a closely follows that of the experimental curve in Figure 1, showing that the numerical differentiation and integration procedures used are self-consistent. The changes in M_n and M_z mirror those of M_w but are more and less pronounced, respectively.

Figure 3b shows the traditional polydispersity ratios M_z/M_w and M_w/M_n computed from Figure 3a. M_w/M_n shows an abrupt change in value after the initiator is added, signaling a bimodality.

It is noted that in computing the data of Figure 1 the value $\alpha = 0$ was used in determining the effective concentration $c = C_p + \alpha C_m$, where c is used to correct for the $2A_2c$ term to the apparent mass in the usual scattering equation. In ref 1 a value of $\alpha = 1$ was used as a first approximation. Although the $2A_2c$ correction to the apparent mass is usually small, it is significant enough in this case that the $\alpha = 1$ value leads to physically implausible negative values of $M_{w,inst}(f)$ over the region $f = 0.25$–0.32.

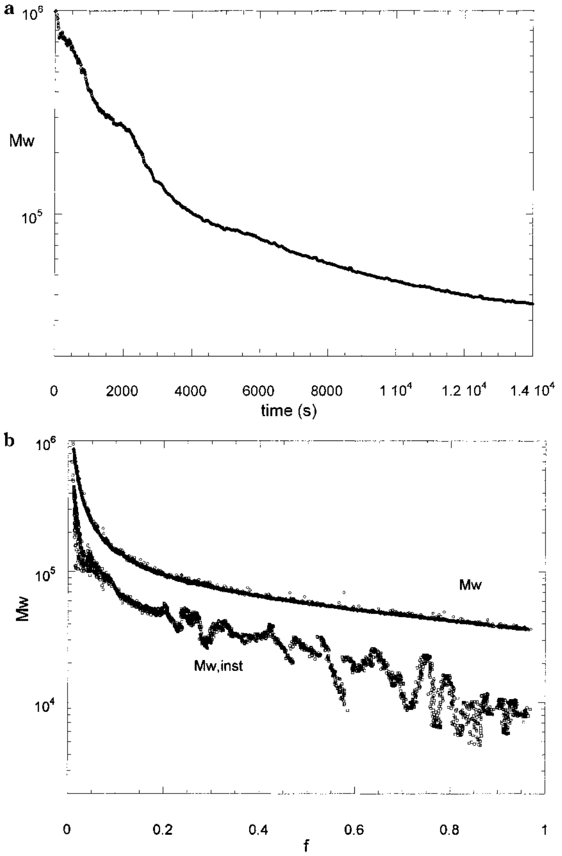

Figure 4. (a) M_w vs t for a PVP reaction, using AIBN as an initiator, which produced a broad unimodal polymer mass distribution. (b) M_w vs f and $M_{w,inst}$ vs f, from the data of (a).

2. A Broad, Unimodal Distribution of PVP. Use of an AIBN initiator led to a very different result for PVP polymerization. The reaction was carried out with 20% vinylpyrrolidinone (VP) in pure water at $T = 70$ °C. The ratio of AIBN to VP, by mass, was 8×10^{-4}. A large variation in $M_w(f)$ was found (Reed and Brousseau, unpublished results). The raw data in the time domain, $M_w(t)$, are shown in Figure 4a. No smoothing was used in these data, which reflects improvements in the experimental data gathering instrumentation and techniques.

Figure 4b shows $M_w(f)$ for the same experiment. These data were subjected to the same type of incremental analysis as the last example, with the resulting $M_{w,inst}(f)$ also shown in Figure 4b. The result for $M_{w,inst}(f)$ shown used the linear fitting over intervals as opposed to end point averaging. Again, there was very little difference between the two methods. One hundred conversion points were fit at a time. Lower numbers of points could also be used but led to noisier results for $M_{w,inst}(f)$.

Histogram representations for the $M_{w,inst}(f)$ curve of Figure 4 at selected conversion points are shown in Figure 5a–c; $f = 0.1$, 0.25, and 0.9. A unimodal distribution, which broadens with increasing conversion, is found. The different mass averages, uncorrected for instantaneous polydispersity, are shown in Figure 6a and the polydispersity indices in Figure 6b. Figure 6b also include the results for the assumed geometric distribution of chains, in the long chain limit (eqs 20 and 22, assuming the condition in eq 27).

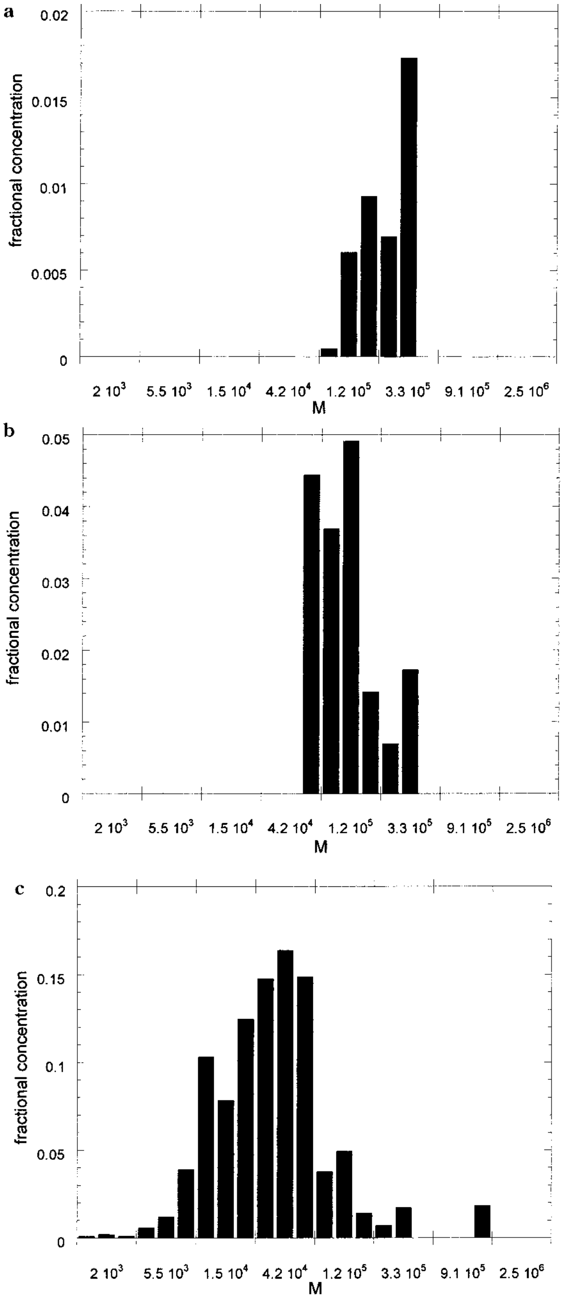

Figure 5. Histograms of mass distributions for different conversion points for PVP polymerization of Figure 4 indicate a broadening, unimodal distribution: (a) $f = 0.1$, (b) $f = 0.25$, and (c) $f = 0.9$.

Other Means of Continuously Computing Polydispersity Online

1. Combination of Light Scattering and Viscosity Data. In ref 1 a first attempt was made to define a polydispersity index by combining the M_w provided by light scattering with the η_r obtained from the viscometer. If η_r is taken to approximate the intrinsic viscosity $[\eta]$, and if a unique relationship between $[\eta]$ and M exists (the so-called Mark–Houwink relationship) over a sufficiently wide range of masses

$$\eta = AM^{\beta} \tag{29}$$

then a certain average of the polymer mass distribution $c(M)$ is measured,

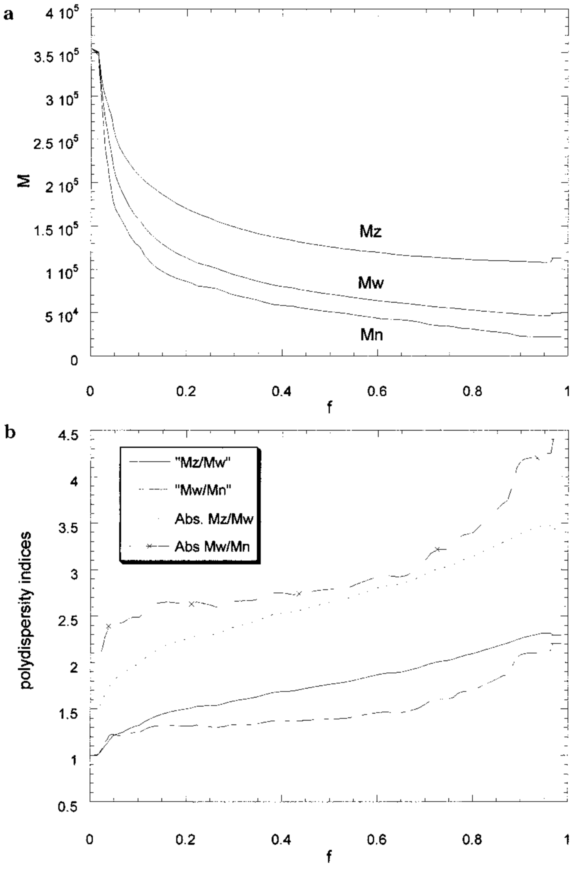

Figure 6. (a) Usual weight averages vs time for broad PVP polymerization, according to eqs 8, 20, and 22, with no correction for instantaneous polydispersity for M_n and M_z in eqs 20 and 22, respectively. (b) Relative polydispersity indices for the broad PVP polymerization. Also shown are the model-dependent absolute polydispersities, assuming the long chain limit values of eq 27 when computing M_n and M_z by eqs 20 and 22, respectively.

$$[\eta] = \frac{A\int M^{\beta} c(M)\,\mathrm{d}M}{\int c(M)\,\mathrm{d}M} \tag{30}$$

where $c(M)\,\mathrm{d}M$ represents the total concentration of a sample in the mass range of M to $M + \mathrm{d}M$. The Mark–Houwink coefficient generally runs from 0.5 for ideal random coils to 2 for rigid rods. Hence, the moment of the distribution measured is related to the weight-average of M^{β} by

$$\langle M^{\beta}\rangle_{\mathrm{w}} = \frac{[\eta]}{A} \tag{31}$$

and taking the ratio $M_{\mathrm{w}}/[\eta]^{1/\beta}$ will yield a measure of the width of a given polymer mass distribution, which depends on β. In order for this procedure to be useful, then, the values of A and β must be known. An advantage of this technique is that both M_{w} and $[\eta]$ can be measured over a wide range of molecular mass. Furthermore, this technique will also be useful for cases where the chain propagation time is not necessarily much shorter than the entire time for a reaction to occur, e.g., in stepwise polymerization. A disadvantage is that it gives a somewhat peculiar polydispersity index, which is not as commonly used compared to $M_{\mathrm{w}}/M_{\mathrm{n}}$ and M_z/M_{w}, and for the special case where $\beta = 1$, it gives no polydispersity information at all, since the M_{η} is proportional to M_{w}.

2. Use of Mean-Square Radius of Gyration and M_{w}. Another approach is to use the relationship between M_{w} and the mean-square radius of gyration $\langle S^2\rangle_z$, which can also be obtained by light scattering. Referring to Zimm's approximation for dilute polymer solutions, in the case where $q^2\langle S^2\rangle_z \ll 1$, the excess Rayleigh scattering ratio $I(q)$ (the sample scattering level minus the solvent scattering) is related to M_{w}, $\langle S^2\rangle_z$, the concentration of polymer C, and the second virial coefficient A_2 via

$$\frac{KC}{I(q)} = \frac{1}{M_{\mathrm{w}}}\left(1 + \frac{q^2\langle S^2\rangle_z}{3}\right) + 2A_2C \tag{32}$$

In the case of dilute solutions where $Q(q)$ is independent of angle, the slope of the above expression yields

$$\text{slope} = \frac{\mathrm{d}(KC/I(q))}{\mathrm{d}q^2} = \frac{\langle S^2\rangle_z}{3M_{\mathrm{w}}} \tag{33}$$

Generally, there is a relationship of the form

$$\langle S^2\rangle = BM^{\alpha} \tag{34}$$

where α runs from $^1/_3$ for dense spherical objects to 0.5 for ideal random coils, ~0.6 for coils with excluded volume, etc., so that the slope is a direct measure of the following moments of the polymer mass distribution

$$3 \times \text{slope} = \frac{B\int M^{\alpha+1}c(M)\,\mathrm{d}M/\int Mc(M)\,\mathrm{d}M}{\int Mc(M)\,\mathrm{d}M/\int c(M)\,\mathrm{d}M} \tag{35}$$

or

$$\text{slope} = \frac{B\langle M^{\alpha}\rangle_z}{3M_{\mathrm{w}}} \tag{36}$$

For the case of ideal coils, the slope is directly proportional to M_z/M_{w}. For coils with excluded volume the slope will be somewhat higher than proportional to M_z/M_{w}. The coefficients B and α for a given type of polymer need to be established independently, e.g., by use of size exclusion chromatography with a multiangle light scattering detector.

An advantage of this technique is that it gives a polydispersity index very close to the commonly used M_z/M_{w} and can be obtained directly from the light scattering data and concentration detector(s). As with the combined viscosity/M_{w} data, it is not limited to reactions in which the chain propagation time is much shorter than the entire reaction time. A limitation is that it can only be used for polymers for which $\langle S^2\rangle_z$ is measurable with conventional detectors; roughly, this means that flexible polymers of mass below about 100 000 g/mol ($\langle S^2\rangle \sim 10$ nm) have unmeasurably small $\langle S^2\rangle_z$ when using conventional light scattering detectors.

Both these latter techniques have been utilized for analyzing polydispersity on a recently submitted work concerning acrylamide polymerization.

Summary

The online technique for polydispersity presented here should be useful for chain growth polymerizations whenever individual chains grow and terminate on a time scale much smaller than the time it takes for significant monomer conversion to occur. A complete, instantaneous weight-averaged mass distribution is found that is an approximation to the true mass distribution. Relative changes in polydispersity, including sequential production of multimodal populations, should be monitorable. Corrections for the instantaneous width of chains produced are also discussed and allow absolute polydispersity to be estimated based on a model appropriate for a given type of polymerization.

It is shown that the technique is robust in detecting a bimodal population and in distinguishing broad, single mode distributions. A challenge will be to develop appropriate algorithms, with effective error analysis, for online use, where the incoming data stream of $M_w(t)$ will have to be continuously averaged and differentiated numerically in real time.

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